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Characterization by NMR of reactants and products of hydrofluoroether isomers, $CF_3(CF_2)_3OCH_3$ and $(CF_3)_2C(F)CF_2OCH_3$, reacting with isopropyl alcohol

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The 3M Company product Novec™ 71IPA DL, a mixture of methoxyperfluorobutane, methoxyperfluoroisobutane and 4.5 wt.% isopropyl alcohol, has been found to be very stable at ambient temperature, producing fluoride at the rate of ~1 ppm/year. Our earlier kinetic and theoretical studies have identified the reaction mechanism. This paper identifies the ^1H and ^{19}F NMR chemical shifts, multiplicities, and coupling constants of reactants and the major products that result from aging the mixture in sealed Pyrex NMR tubes for periods up to 1.8 years at temperatures from 26 °C to 102 °C. Chemical shifts and coupling constants of fluorine and hydrogen atoms on the hydrofluoroethers and isopropyl alcohol are traced through the reactions to their values in the products – esters, isopropylmethyl ether, and HF. These spectral positions, multiplicities, and coupling constants are presented in table format and as figures to clarify the transformations observed as the samples age. Copyright © 2013 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: NMR; ^1H; ^{19}F; hydrofluoroethers; isopropyl alcohol; Novec™ 7100; Novec™ 71IPA

Introduction

Recently, a number of cleaning agent replacements for environmentally undesirable materials have been developed and are currently in use. One specific cleaning agent designed for removing light soils is an azeotrope of methoxyperfluorobutane isomers, C_4F_9–O–CH_3 (Novec™ 7100DL) and isopropyl alcohol (IPA). This solvent combination has been the object of our recent work that addressed the stability of Novec™ 7100DL in the presence of several different concentrations of IPA. Novec™ 71IPA DL is an isomeric mixture containing the *normal*-isomer, $CF_3(CF_2)_3OCH_3$, the iso-isomer, $(CF_3)_2CFCF_2OCH_3$ in ~40/60 ratio, a *chiral* isomer (<0.025 wt.%), and IPA at ~4.5 wt.%. Density functional theory calculations[1] for the reaction of the two major isomers with IPA predicted that isomeric acyl fluorides, $C_3F_7CO(F)$, isopropylmethyl ether (IME), $(CH_3)_2CH$–OCH_3, and HF are produced in the rate-determining step (Eqn (1)). Our predicted and measured thermodynamic activation parameters ($\Delta H^{\ddagger}_{pred.} = 24.6$ kcal/mol and $\Delta H^{\ddagger}_{obs.} = 25$ kcal/mol) are indicative of a slow reaction at ambient temperatures. The second, and faster, reaction occurs between acyl fluoride and another molecule of IPA, producing isomeric isopropyl esters and a second molecule of HF (Eqn (2)).[1]

$$C_4F_9OCH_3 + (CH_3)_2C(H)OH \overset{slow}{\rightarrow} C_3F_7C = O(F) + (CH_3)_2C(H)OCH_3 + HF \quad (1)$$

$$C_3F_7C = O(F) + (CH_3)_2C(H)OH \overset{fast}{\rightarrow} C_3F_7COOCH(CH_3)_2 + HF \quad (2)$$

We have been unable to observe the ^{19}F NMR resonance for the acyl fluorides in the region +10 to +60 ppm[2] because of their rapid reaction with IPA. In general, acyl halides, in the presence of alcohols, react rapidly at ambient temperatures to form esters[3] with rate constants on the order 10^{-3}/s. Our measured rate constants[1] for the slow step are between 10^{-15} and 10^{-12}/s for temperatures of 26 to 90 °C. Thus, the rate constant for the reaction in Eqn (2), 10^{-3}/s, would be between 10^9 and 10^{12} times faster than that in Eqn (1). In our multiple-pulse experiments – where samples were examined at room temperature after removal from their respective heating media – the lifetime of the acyl fluoride was too short for NMR detection.

The identification of a single ^{19}F resonance in the range −140 to −180 ppm attributable to HF is also problematic. Interaction

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between the HF and the OH of IPA and/or water (if present) leads to complex equilibria involving H_2F^+ and/or $(HF)_nF^-$ species where *n* is between 1 and 3. These broad resonances change position and intensities as a function of heating time and cannot be specifically attributed to non-complexed HF as the dominant molecular entity.[4]

Although NMR was used to measure rates at a variety of temperatures and reactant concentrations in our previous study,[1] few spectral details were included. This current paper reports ^{19}F and ^{1}H NMR chemical shifts and coupling constants of the two major methoxyperfluorobutane isomers and 4.5 wt.% IPA, and the major products of their reaction at 90 °C in a mixture that was aged for 363 days.

Experimental

Instrumentation

Several NMR spectrometers were used in measuring ^{1}H and ^{19}F signals. A Bruker 400 MHz was used for multiple-pulse ^{19}F measurements, and a Burker 500 MHz was used for multiple-pulse ^{1}H measurements including COSY and TOCSY experiments. An Anasazi EFT 60 was used to measure T_1 values of fluorine atoms in the two major isomers of methoxyperfluorobutane.

Materials

The following chemicals and materials were used in the preparation of the samples and standards needed for this study.

1. Novec™-7100 Lot No. 24448, Novec™7100DL[5] Lot Nos. 20221 and 20224, and Novec™71IPA Lot Nos. 22038 and 22121 provided by 3M Company (Saint Paul, MN 55144-1000, USA. A typical analysis provided by 3M Company shows that the three Novec™7100 isomers and IPA comprise ~99.84 wt.% of the mass of Novec™ 71IPA, the remaining 0.16 wt.% of the sample is a proprietary composition.
2. 2-Propanol (IPA), 99.5%; anhydrous, <0.005% water purchased from Sigma-Aldrich (Atlanta, GA 303553-5182, USA) Batch No. 04750TE.
3. No vendor could be found to provide an authentic sample of IME to compare its resonances to those present in our samples. See Eqn (1). Therefore, IME was synthesized using the Williamson reaction. An approximate 2 : 1 molar excess of powdered sodium isopropoxide (Alfa Aesar (Ward Hill, MA 01835, USA) Stock No. 89446 and Lot No. C06U026) was mixed with methyl iodide (Fisher Scientific Pittsburgh, PA 15275, USA (Certified M2121-100, Lot No. 084930)) under vacuum conditions. After 3 days at room temperature, the volatile IME was vacuum transferred to an NMR tube using liquid nitrogen. The ^{1}H NMR spectrum was recorded at 300 MHz in the same medium used for NMR measurements of aged samples (i.e. 4.5 wt.% IPA in Novec™ 7100DL). The chemical shifts matched. They are as follows: $(CH_3)_2$ doublet at 1.1 ppm, CH septet at 3.4 ppm, and OCH_3 singlet at 3.3 ppm, with the intensities matching the expected pattern of 6 : 1 :
4. Chloroform-*d*, 99.8% D, stabilized with silver foil, 0.03 v/v% TMS, obtained from Acros Organics (Pittsburgh, PA, USA), Code No. 368651000, Lot No. A0274197.
5. Fluorotrichloromethane, $CFCl_3$, 99+%, purchased from Sigma-Aldrich (Atlanta, GA 30353-5182, USA) Stock No. 254991-800ML, Batch No. 03706ME.
6. Acetone-d_6, 99.9%D, obtained from Norell, Inc. (Landisville, NJ 08326, USA) Lot No. 8276.
7. Special Pyrex 5-mm NMR tubes procured from Norell, Inc. (Landisville, NJ 08326, USA) Part No. S-5-300-8 constricted (for sealing).
8. Tetramethylsilane, 99.9+%, NMR grade, A.C.S. reagent, purchased from Sigma-Aldrich (Atlanta, GA 30353-5182, USA) Stock No. T24007-100G, Batch No.11418EE.
9. Hamilton Company (Reno, NV 85920-0012, USA) glass syringes with stainless steel needles were used in the preparation of samples.
10. Melting point capillary tubes used for NMR standards and deuterium lock were procured from Kimax (Vineland, NJ 08362-1502, USA), Stock No. 34500 99, 1.5–1.8 × 100 mm.

Sample preparation

NMR samples

Samples for NMR included both new and aged Novec™ 7100DL and new and aged mixtures of Novec™ 7100DL with IPA. Because IPA is hygroscopic, all samples were prepared in a nitrogen-purged, dry box.[1] The mixtures ranged from 51.0 to 97.25 wt.% of methoxyperfluorobutane isomers with the remainder being IPA.

The NMR test samples, with sealed capillaries[1] containing acetone-d_6 or $CDCl_3$ used for lock signals, were prepared and attached to a vacuum line, chilled with either liquid nitrogen or a dry ice/alcohol slush, evacuated, back filled with 150 Torr O_2, and sealed with a torch. The addition of purified oxygen provided a paramagnetic material to shorten the NMR longitudinal relaxation time (T_1) of hydrogen and fluorine nuclei. The samples were sealed with a torch, instead of capped, to permit long-term heating of the samples without loss of volatile components. At appropriate time intervals, samples were removed from the heating medium, and ^{1}H and ^{19}F multiple-pulse experiments were performed. After analyses, the NMR test sample was returned to the heating medium to continue aging.

Data collection

To avoid potential reactions between the components of Novec™ 7100DL and a solvent, or with internal standards, such as TMS and $CFCl_3$, the NMR tubes used in the aging experiments contained only the neat liquid reactants, Novec™7100DL and IPA. This resulted in very intense NMR signals. In addition, the reactions were very slow. The combination made it impossible to measure the disappearance of reactants in a reasonable time. That is, the uncertainty in the intensity measurement was larger than the intensity difference achieved over, for example, a period of a month at 90 °C. However, it was possible to monitor the growth of product signals above base line by increasing the signal-to-noise ratio through the use of multiple-pulse experiments. To avoid saturating these weak signals, it was necessary to determine the longitudinal relaxation times, T_1, for the ^{19}F nuclei in question. To determine the optimum pulse angle and pulse delay, the Ernst equation was employed. Values of T_1 for samples of the hydrofluoroethers were determined by the inversion–recovery Fourier transform method for samples with and without O_2 present. The results are shown in Table 1.

The ^{1}H and ^{19}F NMR chemical shift scales were referenced to 3.700 ppm for the methoxy group of $(CF_3)_2CFCF_2OCH_3$ and −81.660 ppm for the perfluoromethyl group of $CF_3CF_2CF_2CF_2OCH_3$. The reasons for these choices are as follows: First, the values were consistent with those in the 3M data base, which were referenced

Table 1. Longitudinal relaxation times of ^{19}F NMR resonances for Novec™ 7100 recorded at 56.46 MHz

Chemical species	T_1 with O_2 (s)	T_1 without O_2 (s)
$(\mathbf{CF_3})_2$ iso-isomer	1.7	6.8
$\mathbf{CF_3}$ *n*-isomer overlapping –$\mathbf{CF_2}$–OCH_3 iso-isomer	1.7	6.3
–$\mathbf{CF_2}$–OCH_3 *n*-isomer	1.7	6.1
–$\mathbf{CF_2}$–$\mathbf{CF_2}$– *n*-isomer overlapping peaks	1.8	7.2
C–**F** iso-isomer	2.5	10.2

to internal TMS and $CFCl_3$ signals; and second, the ^{1}H and ^{19}F chemical shifts of reactants and products remained unchanged over 411 days at 90 °C. During this experiment, only 0.27% of the starting material was consumed. This small change in the composition of the solution was insufficient to change the bulk magnetic susceptibility of the sample.

Results and Discussion

Usually ethers are unreactive in the presence of organic compounds, and so they are often used as solvents for reactions. Classic reactions of ethers include the following: (i) the oxidation of ethers in air to form peroxides, (ii) interaction with strong acids, such as HBr, to produce alkyl halides and alcohols, and (iii) Lewis acid–base interactions, such as the complex formed between BF_3 and diethyl ether, called the BF_3:etherate.

The Material Safety Data Sheets, created by 3M Company for Novec™ 71IPA and Novec™ 7100, suggest that these materials are stable below 300 °C. A colorimetric test for peroxide was conducted at room temperature and up to the boiling point for Novec™ 7100 on samples aged for several weeks.[6] These tests were all negative. Testing was also run with older samples of Novec fluids that had been stored at room temperature for 1 year or more, and again, no detectable level of peroxide was found. Furthermore, thermal degradation above 160 °C of related compounds, for example, hydrofluoropolyethers and C_4F_9–OC_2H_5 studied by Marchionni *et al.*[7] in air, never formed peroxides but did include nonclassical ether reaction products, such as perfluorinated acid fluorides and CO_2. In our work, there was no evidence of peroxide formation in aged sealed mixtures of IPA and Novec™ 7100 heated at temperatures as high as 102 °C for periods up to 632 days in a partial pressure of 150 Torr O_2. Additionally, the Novec fluids have been in use for 16 years, and no one, including the Smithsonian,[8] has reported issues with peroxide formation.

To investigate the reaction of Novec™ 71IPA with strong acids, HCl (g) and HBr(g) were separately added to Novec™ 71IPA. No alkyl halides or methanol was detected by NMR as would have been expected of classical ether reactions with strong acids. However, IME and esters were found, and their rates of formation from the reaction of the two isomers of methoxyperfluorobutane and IPA (i.e. Eqn (1) and Eqn (2)) increased by a factor of two. It is believed the reaction described in Eqn (1) is *catalyzed* by the strong acids, as opposed to the acids serving as reagents typical of classic ether reactivity.

Another case of a possible catalytic effect – this time in a Lewis acid–base interaction in the presence of AlF_3 – was discussed in a quantum mechanical study of the decomposition of the perfluoroethers, CF_3OCF_3 and $CF_3CF_2OCF_2CF_3$. The AlF_3 formed the etherate-like complexes, AlF_3:$O(CF_3)_2$ and AlF_3:$O(C_2F_5)_2$, which are more typical of classic ether reactions.[9]

In short, the degradation of the two major isomers of methoxyperfluorobutane, described herein, do not belong to any of the classic ether reactions up to 100 °C. The high activation barrier of 25 kcal/mol is responsible for the long-term ambient stability of Novec™71IPA.

As discussed previously, although the methoxyperfluorobutane isomers are very stable at ambient conditions, they do react with IPA when aged at elevated temperatures, albeit slowly. The following sections recount the details of our NMR findings regarding chemical shifts, multiplicity, and coupling constants attributable to reactants and major products in aged samples. The figures presented later show both the NMR signal of atoms in the starting material and that of the same atom, or atoms, as they appear in the reaction products. Finally, the correlations achieved using a ^{1}H COSY experiment are presented.

^{19}F Spectral Assignments

All of the ^{19}F resonances shown in Figs 1 and 2 were collected using a Bruker 400 operating at 376.463 MHz on a sample of Novec™71IPA aged for 363 days at 90 °C utilizing 1433 scans and the Bruker pulse experiment *zgfhigqn*. The deuterium lock signal was provided by inserting a sealed capillary tube, containing acetone-d_6, $CFCl_3$, and C_6H_6, inside the NMR tube. In Figs 1 and 2, the lower spectrum is of the methoxyperfluorobutane isomer, and the upper spectrum is that of its corresponding isopropyl ester. See Eqn (2).

The iso-isomer in Novec™ 7100 – Fig. 1

The $\mathbf{CF_3}$ groups are converted from a doublet of triplets ($^3J_{FF} = 5.8$ Hz and $^4J_{FF} = 9.8$ Hz) centered at −73.84 ppm to a doublet ($^3J_{FF} = 7.3$ Hz) centered at −74.92 ppm. The **CF** multiplet shifted from −187.38 ppm to a septet centered at −181.48 ppm ($^3J_{FF} = 7.3$ Hz). The –$\mathbf{CF_2}$ doublet

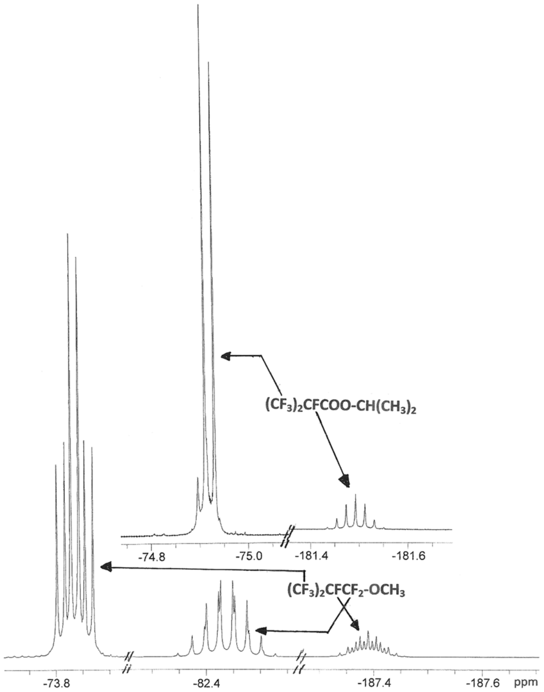

Figure 1. The ^{19}F NMR spectrum of: methoxyperfluoroisobutane (lower) and isopropylperfluoroisobutyrate (upper). Each tie mark within a spectral segment represents a change in chemical shift of 0.05 ppm.

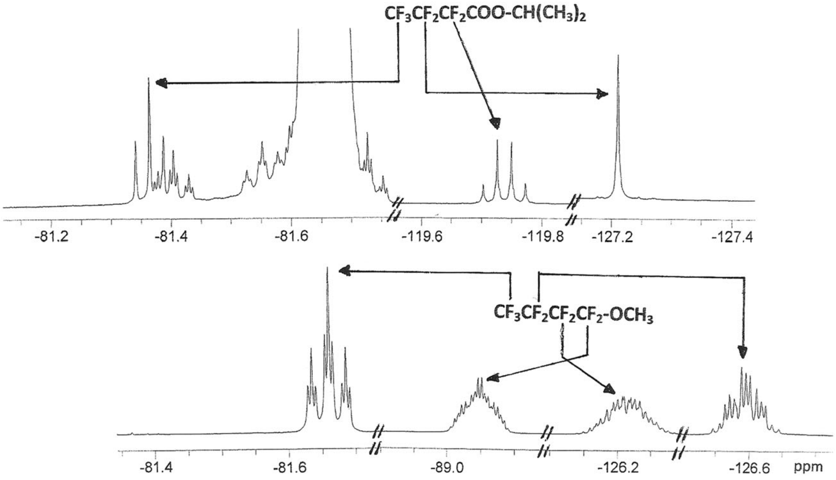

Figure 2. The ^{19}F NMR spectrum of methoxyperfluorobutane (lower) and isopropylperfluorobutyrate (upper). Each tie mark within a spectral segment represents a change in chemical shift of 0.05 ppm.

of septets centered at −82.44 ppm ($^3J_{FF} = 8.5$ Hz and $^4J_{FF} = 9.8$ Hz) does not have a corresponding resonance in the ester because the carbon atom in the CF$_2$ group is transformed to a carboxylate (–**C(O)–O**–). The splitting shown at −82.44 ppm is dependent on how carefully the spectrometer is shimmed. A symmetrical octet is otherwise obtained.

The *normal*-isomer in Novec™ 7100 – Fig. 2

The **CF$_3$** group, a triplet of triplets at −81.66 ppm ($^5J_{FF} = 2.2$ Hz and $^4J_{FF} = 9.6$ Hz) converts to a triplet at −81.36 ppm ($^4J_{FF} = 8.7$ Hz) when the isopropyl ester is formed. No vicinal three-bond couplings were detected. Doblier[10] has reported fluorine–fluorine coupling constants for perfluoroalkanes and concluded that, 'vicinal F–F coupling constants in perfluoroalkanes are often very small, virtually negligible in comparison to longer-range couplings'. The small triplet of triplets signal that overlaps the ester triplet in the upper spectrum in Fig. 2 is due to the ^{13}C satellite of the very strong resonance of the **CF$_3$** group of the *normal*-ether isomer. The satellite to the right of the strong resonance is not shown in the figure, but the $^1J_{CF}$ of 286.6 Hz was measured and is consistent with the range for **CF$_3$** groups found on page 138 of Doblier.[10]

The **CF$_2$** groups in the reactant chain are all multiplets, and their resonances occur at −89.05, −126.21, and −126.59 ppm as seen in Fig. 2. The fluorine atoms on the corresponding **CF$_2$** groups in the product are as follows: a quartet centered at −119.74 ($^4J_{FF} = 8.7$ Hz) and a single resonance centered at −127.21 ppm. The later resonance appears as a broadened singlet resulting from coupling interactions being of the $^3J_{FF}$ variety.

^{1}H Spectral Assignments

All of the resonances shown in Figs 3–5 were obtained with a Bruker 500 operating at 500.023 MHz on the same sample of Novec™71IPA discussed previously. The Bruker pulse experiment *zg30* was used for 128 scans.

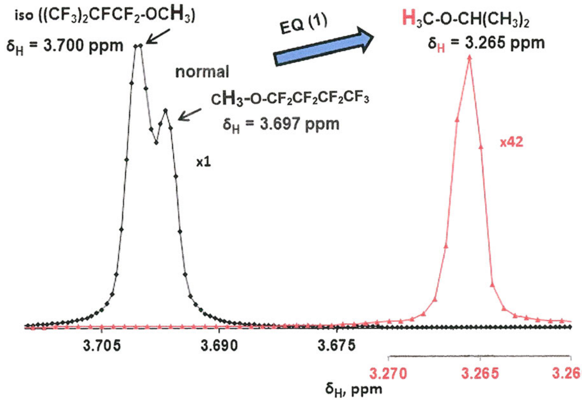

Figure 3. The ^{1}H NMR spectrum of the methoxy groups of methoxyperfluoroisobutane and methoxyperfluorobutane (left) being converted to the methoxy group on isopropylmethyl ether (right).

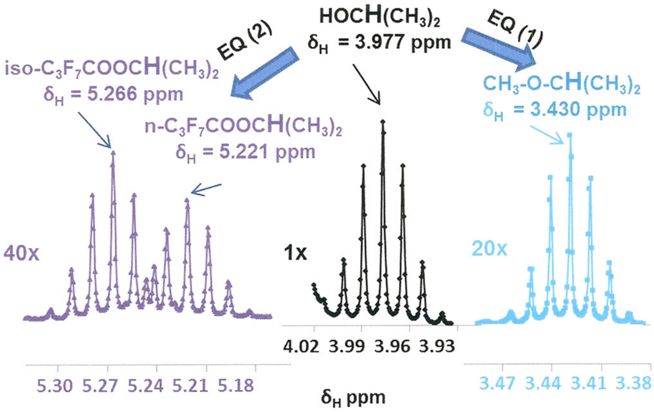

Figure 4. The ^{1}H NMR spectrum of the methine hydrogen on IPA (center) as it is converted to the methine hydrogen on isopropylmethyl ether (right), and to the methine hydrogen on each of the esters, isopropylperfluoroisobutyrate and isopropylperfluorobutyrate (left).

Normal and iso isomers in Novec™ 7100 – Fig. 3

The methoxy hydrogen atoms on each of the two methoxyperfluorobutane isomers appear as single overlapping resonances at 3.700 and 3.697 ppm. The intensity ratio, iso/normal, of 61/39 ± 1 was determined by deconvolution of the data in Fig. 3 and by using the integrated ^{19}F intensities of the

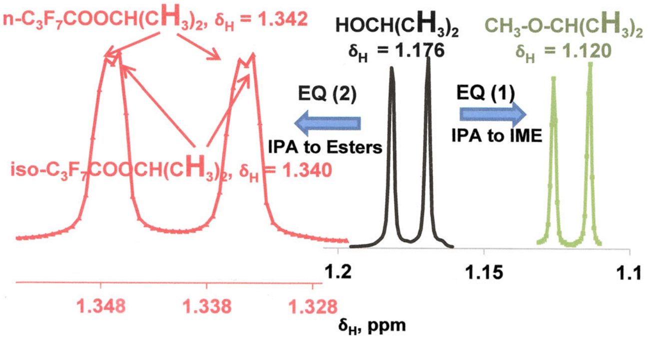

Figure 5. The ^1H NMR spectrum of the methyl groups on isopropyl alcohol (center) as they are converted to the methyl groups on isopropylmethyl ether (right), and to the methyl groups on the esters, isopropylperfluoroisobutyrate and isopropylperfluorobutyrate (left).

seven resonances in the lower portion of Figs 1 and 2. The details of the second method are found in the Supporting Information. The reaction in Eqn (1) shows that the methoxy $\mathbf{CH_3}$ groups on both isomers end up as the methoxy $\mathbf{CH_3}$ group on the product, isopropylmethyl ether, with a chemical shift of 3.265 ppm.

Isopropyl alcohol in Novec™71IPA – Figs 4 and 5

The reaction in Eqn (2) indicates that the isomeric acid fluorides each react with a molecule of IPA yielding the corresponding iso and normal esters. Figure 4 focuses on the methine hydrogen atom in IPA as its chemical shift changes depending on whether it is part of the isomeric ester structures, Eqn (2), or the IME structure, Eqn (1). The methine hydrogen of IPA starts off as a septet at 3.977 ppm ($^3J_{HH} = 6.3$ Hz) and is transformed to the iso-ester as a septet at 5.266 ppm ($^3J_{HH} = 6.3$ Hz) and to the *normal*-ester as a septet at 5.221 ppm ($^3J_{HH} = 6.3$ Hz). In transitioning to IME, the IPA methine hydrogen is found as a septet at 3.430 ppm ($^3J_{HH} = 6.3$ Hz).

Figure 5 focuses on the isopropylmethyl groups in IPA as their chemical shift changes from IPA either to that of the isomeric ester structures or to that of IME. Their resonance starts off as a doublet at 1.176 ppm ($^3J_{HH} = 6.2$ Hz) and is transformed to the iso-ester as a doublet at 1.340 ppm ($^3J_{HH} = 6.3$ Hz) and to the *normal*-ester as a doublet at 1.342 ppm ($^3J_{HH} = 6.3$ Hz), and to a doublet at 1.120 ppm ($^3J_{HH} = 6.3$ Hz) in IME.

NMR Correlation SpectroscopY (COSY)

A two-dimension, ^1H NMR COSY experiment[11] was performed at 500.023 MHz on the same Novec™ 71IPA sample as discussed previously. Figure 6 shows the data. In the plot, the proton NMR spectrum appears on each of the orthogonal axes. Peaks with the same chemical shift on each axis intersect on the plot diagonal. Off-diagonal signals correspond to ^1H–^1H homonuclear spin couplings. A PDF file, with scale expansion capability, is available in the Supporting Information.

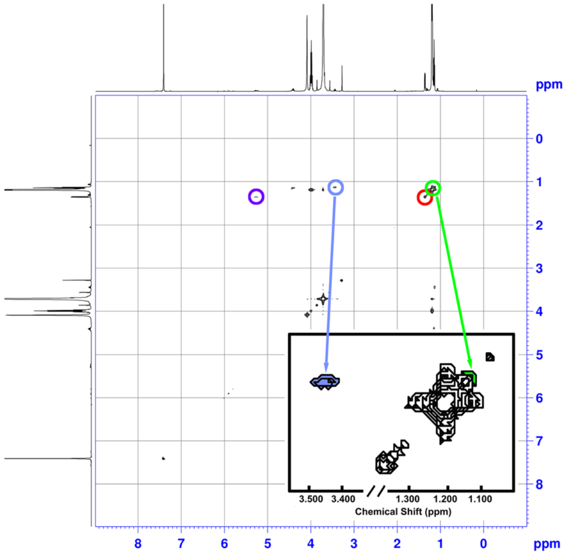

Figure 6. The ^1H COSY data taken on a sample of NOVEC™71IPADL that had been heated at 90 °C for 365 days.

Three pairs of coupled protons are depicted in Fig. 6. The first two pairs, circled in red and purple, are due to the isopropyl groups on the two isomeric esters (Eqn (2)). Methyl resonances (centered at 1.340 and 1.342 ppm), circled in red, are doublets split by the methine hydrogens. The methine resonances (centered at 5.266 and 5.221 ppm), circled in purple, are septets split by the methyl hydrogens. The larger doublet centered at 1.340 ppm and the septet centered at 5.266 ppm have been assigned to the most abundant isomeric ester, the iso-isomer. Their companion resonances belong to the *normal*-isomeric ester. We refer the reader to the expanded scale spectra illustrated in red in Figs 4 and 5. The integration of the methyl and methine resonances are in a 6 : 1 ratio.

The third pair of coupled protons in Fig. 6, circled in green for the doublet and cyan for the septet, deal with isopropyl methyl ether, the product created in Eqn (1). The methyl hydrogens and the methine hydrogen on the isopropyl group of IME appear as a doublet, centered at 1.120 ppm, and a septet centered at 3.431 ppm, respectively. They also integrate in the ratio 6 : 1.

Although the COSY data were useful in identifying the off-diagonal peaks of the esters and IME, it did not relate the protons of methoxy hydrogens in IME (–O–CH_3) to any of the methyl or methine resonances. A selective TOCSY experiment was performed, but it only confirmed the COSY results without adding anything new about the methoxy group in IME.

Conclusion

The ^{19}F and ^1H NMR chemical shifts, coupling constants, and multiplicities of the components (Novec™ 7100DL and IPA) that make up Novec™ 71IPA DL were identified and measured. These components are very stable together but have been found to react with each other very slowly producing hydrogen fluoride, IME, and two esters, isopropyl perfluoroisobutyrate and isopropyl perfluorobutyrate at rates of ~1 ppm/year at a laboratory temperature of 20°C. The chemical shifts, coupling constants, and multiplicities of these products have also been determined. The detailed NMR spectra are shown, and the measurements are summarized in Table 2. A ^1H COSY experiment was used to show the association of the methyl and methine hydrogens in the products of the reaction. An authentic sample of IME was synthesized using the Williamson synthesis. The chemical shifts, thus obtained, were found to be identical to those found in the aged samples of Novec™71IPA DL.

Table 2. Summary of NMR data for reactants and primary products, Eqns (1) and (2)

Peak	Compound (isomer)	Nuclei	Reactant δ (ppm)	Reactant multiplicity (coupling constant, Hz)[c]	Product δ (ppm) of ester	Product multiplicity (coupling constant, Hz)[c]
$(\mathbf{CF_3})_2$–CF–CF$_2$–OCH$_3$	iso-Novec™ 7100	^{19}F	−73.84[a]	d($^3J_{FF} = 5.8$)/t($^4J_{FF} = 9.8$)	−74.92[a]	d($^3J_{FF} = 7.3$)
(CF$_3$)$_2$–**CF**–CF$_2$–OCH$_3$	iso-Novec™ 7100	^{19}F	−187.38[a]	m	−181.48[a]	sept($^3J_{FF} = 7.3$)
(CF$_3$)$_2$–CF–$\mathbf{CF_2}$–OCH$_3$	iso-Novec™ 7100	^{19}F	−82.44[a]	d($^3J_{FF} = 8.5$)/sept($^4J_{FF} = 9.8$)	Formed HF −140 to −150[a]	Broad peak due to exchange
$\mathbf{CF_3}$–CF$_2$–CF$_2$–CF$_2$–OCH$_3$	*n*-Novec™ 7100	^{19}F	−81.66[a]	t($^5J_{FF} = 2.2$)/t($^4J_{FF} = 9.6$)	−81.36[a]	t($^4J_{FF} = 8.7$)
CF$_3$–$\mathbf{CF_2}$–CF$_2$–CF$_2$–OCH$_3$	*n*-Novec™ 7100	^{19}F	−126.59[a]	m	−127.21[a]	s, broad
CF$_3$–CF$_2$–$\mathbf{CF_2}$–CF$_2$–OCH$_3$	*n*-Novec™ 7100	^{19}F	−126.21[a]	m	−119.74[a]	q($^4J_{FF} = 8.7$)
CF$_3$–CF$_2$–CF$_2$–$\mathbf{CF_2}$–OCH$_3$	*n*-Novec™ 7100	^{19}F	−89.05[a]	m	Formed HF −140 to −150[a]	broad peak due to exchange
HO–CH–$(\mathbf{CH_3})_2$	IPA to iso-ester and *n*-ester	^{1}H	+1.176[b]	d($^3J_{HH} = 6.2$)	iso- +1.340[b] *n*- +1.342[b]	d($^3J_{HH} = 6.3$) d($^3J_{HH} = 6.3$)
HO–**CH**–(CH$_3$)$_2$	IPA to iso-ester and *n*-ester	^{1}H	+3.977[b]	sept($^3J_{HH} = 6.1$)	iso- +5.266[b] *n*- +5.221[b]	sept($^3J_{HH} = 6.3$) sept($^3J_{HH} = 6.3$)
HO–CH–(CH$_3$)$_2$	IPA to iso-ester and *n*-ester	^{1}H	+4.026[b]	s, broad	Formed HF −140 to −150[a]	broad peak due to exchange
Peak	Compound (isomer)	Nuclei	Reactant chemical shift (ppm)	Reactant multiplicity (coupling constant, Hz)[c]	Product chemical shift (ppm) of IME	Product multiplicity (coupling constant, Hz)[c]
HO–CH–$(\mathbf{CH_3})_2$	IPA to IME	^{1}H	+1.176[b]	d($^3J_{FF} = 6.1$)	+1.120[b]	d($^3J_{HH} = 6.1$)
HO–**CH**–(CH$_3$)$_2$	IPA to IME	^{1}H	+3.977[b]	sept($^3J_{FF} = 6.2$)	+3.430[b]	sept($^3J_{HH} = 6.1$)
HO–CH–(CH$_3$)$_2$	IPA to IME	^{1}H	+4.026[b]	s, broad	formed HF	
(CF$_3$)$_2$–CF–CF$_2$–O$\mathbf{CH_3}$	iso-Novec™ 7100 to IME	^{1}H	iso- +3.700[b]	s	+3.265[b]	s
CF$_3$–CF$_2$–CF$_2$–CF$_2$–O$\mathbf{CH_3}$	*n*-Novec™ 7100 to IME		*n*- +3.697[b]	s	+3.265[b]	s

IPA, isopropyl alcohol;IME,isopropylmethyl ether.

[a] Peaks referenced to −81.66 ppm associated with the terminal fluorinated methyl group CF$_3$ of the *n*-isomer.

[b] Peaks referenced to 3.700 ppm associated with the methoxy hydrogens (OCH$_3$) of the Novec™-7100 iso-isomer.

[c] Multiplicities are given as 's' for singlet, 'd' for doublet, 't' for triplet, 'q' for quartet, 'sept' for septet, and 'm' for multiplet.

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