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2,2,3,3,4,4,4-Heptafluorobutyl Acetate: Transesterification Reaction of 2,2,3,3,4,4,4-Heptafluoro-1-Butanol and Isopropyl Acetate—Side-Product Composition †

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Abstract: As the object of investigation in the present study, reactive distillation based on the transesterification of isopropyl acetate (IPAc) and 2,2,3,3,4,4,4-heptafluorobutanol (HFBol) under acidic conditions is addressed. This process aims to obtain 2,2,3,3,4,4,4-heptafluorobutyl acetate (HFBAc), which is used in the production of non-aqueous electrolytes, ethyllithium sulphate, charge retention medium, ultraviolet light-absorbing oligomers, etc. Through a combination of NMR spectroscopy and GC-MS, it was determined that during the process, the following were primarily formed in the system: target HFBAc and the by-product, isopropanol. The following side-products were identified: di-isopropyl ether, acetic acid, water, and 2,2,3,3,4,4,4-heptafluorobutyl isopropyl ether (HFB-IPEth). No bis(1H,1H-heptafluorobutyl) ether or acetic anhydride were identified in the system. For HFBol, HFBAc and HFB-IPEth the ^{1}H, ^{19}F and $^{13}C\{^{19}F\}$), ^{19}F-^{19}F COSY NMR, and mass spectra were reported in this study.

Keywords: 2,2,3,3,4,4,4-heptafluorobutanol; isopropyl acetate; transesterification; reactive distillation; side-products; di-isopropyl ether; 2,2,3,3,4,4,4-heptafluorobutyl isopropyl ether

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1. Introduction

As the object of investigation in the present study, the reactive distillation (RD) process based on the transesterification of isopropyl acetate (IPAc) and 2,2,3,3,4,4,4-heptafluorobutanol (HFBol) under acidic conditions is addressed. This process aims at obtain 2,2,3,3,4,4,4-heptafluorobutyl acetate (HFBAc), which is used in pharmaceutical aerosol compositions to reduce particle adhesion to can walls, inhibit particle flocculation, and preventing the creaming of the suspension [1]. It is also used in the production of red-absorbing dyes for imaging and sensing and red-shifted Förster resonance energy transfer (FRET) quencher dyes [2]. It can also be used as a more environmentally friendly analogue of perfluorocarbons for the plasma etching of SiO_2 films for semiconductor production [3] and similar processes.

Thus far, information on methods of HFBAc production is practically absent in the literature. A number of sources mention its formation as a side-product during the synthesis of 1,1,1,2,2,3,3-heptafluoro-4-iodobutane (HFBAc ≈ 4%) [4], heptafluorobutyl methacrylate (HFBAc ≈ 1.3%) [5], and a diacetate ester of aldehydrol [6].

Methods for the synthesis of HFBol esters are generally better researched, with well-known methods based on reactions with anhydrides (e.g., isobutyric [7] and methacrylic) [8],

halogen anhydrides (e.g., 2-propenoyl chloride) [9], various acids [10–14] (including electrochemical methods at room temperature without the usage of catalysts) [15], methyl and ethyl esters of halogen-substituted acids [16], and methyl methacrylate followed by the polymerization of heptafluorobutyl methacrylate by a double bond [17].

To select suitable conditions for the synthesis and purification of HFBAc, it is necessary to control the composition of the reaction mixture while varying parameters such as time processing, process temperature, and the composition and ratio of initial reagents. At the same time, quantitative analysis is quite difficult without understanding the qualitative composition, including the composition of reaction side-products and their formation conditions. As a number of different side-products are formed during the transesterification reaction between IPAc and HFBol, the aim of the present study is a qualitative analysis of the reaction products via a combination of gas chromatography–mass spectrometry (GC-MS) and nuclear magnetic resonance (NMR) spectroscopy.

2. Materials and Methods

In the present study, the RD process with the initial equimolar ratio of reagents was carried out in batch mode at atmospheric pressure, and the temperature of the reaction varied from 95 to 105 °C. The identification of by-products requires a significant (detectable) amount of the last one in the reaction mixture. Thus, the process was carried out under "harsh" acidic conditions; H_2SO_4 was used as a catalyst (up to ≈0.2 mol. fr. in the reaction area). Information on the compounds used in this study is presented in Table 1.

Table 1. Specifications of the compounds used.

Chemical Name	CAS-No	Molar Mass M/g·mol^{-1}	Supplier	Initial Mass Fraction Purity	Purification in Laboratory	Mass Fraction After Purification (GC [a])
2,2,3,3,4,4,4-heptafluorobutanol	375-01-9	200.05	P&M Invest	0.60–0.90	Heteroazeotropic distillation; distillation	≥0.998
Isopropyl acetate	108-21-4	102.1	ECOS-1	0.998	none	-
Sulfuric acid	7664-93-9	98.07	Merk	0.98	none	-
Dimethyl sulfoxide-d6	2206-27-1	84.17	Solvex-D	0.998 atom % D	none	-

[a] Gas chromatography—flame ionization detector (Agilent 6890 N equipped with a Restek RTX-1701 RK12054 capillary column;Agilent Technologies, Inc., Wilmington, DE, USA).

Mass spectra were determined using the gas chromatograph Maestro-αMS with a quadrupole mass spectrometer (Interlab, Moscow, Russia). Chromatographic separations were carried out using a capillary column SCI-5MS (30 m × 0.25 mm i.d., film thickness 0.25 μm; MEGA S.r.l, Legnano, Italy). The injector temperature was set at 250 °C in split mode (split ratio 1/100); the column (oven) temperature was 35 °C (4 min). The carrier gas was helium at a constant flow of 1.0 mL·min^{-1}. The ion source temperature and the interface temperature were 230 °C and 250 °C, respectively. The spectra were obtained in SCAN mode. The electron impact ionization energy was 70 eV, and the mass range was *m/z* 29–300. The Bruker Avance II—300 MHz NMR spectrometer (Bruker Corp., Billerica, MA, USA) was used to obtain ^{1}H and ^{19}F spectra of studied samples at the frequencies of 300.211 MHz and 282.499 MHz, respectively, using internal deuterium lock. The QOne AS400 quantum-I Plus—400 MHz NMR spectrometer (QOneTec, Wuhan, China) was used to obtain ^{13}C{^{19}F}, ^{19}F and ^{19}F-^{19}F COSY spectra of studied samples at the frequencies of 100.549 MHz and 376.263 MHz, respectively, using internal deuterium lock. Tetramethylsilane and trichlorofluoromethane were used as external references. Dimethyl sulfoxide-d6 (d-DMSO) was used as a solvent. Mass Comparator MC-1000 (A&D Company Ltd, Tokyo, Japan) was used to measure sample weight.

3. Results and Discussion

The RD process considered in this study is based on the transesterification reaction of IPAc and HFBol under acidic conditions. According to preliminary experimental data, in addition to the two reagents, target product HFBAc and by-product isopropanol (IPol), a number of side-products were found to be present in the reaction mixture. Preliminary studies of the reaction mixture showed the presence of water in the samples. It follows that the presence of alcohols (by-product—IPol and reagent—HFBol) in the system suggests their possible intermolecular dehydration (potentially, the formation of up to three ethers—2,2,3,3,4,4,4-heptafluorobutyl isopropyl ether (HFB-IPEth), di-isopropyl ether (IPEth) and bis(1H,1H-heptafluorobutyl) ether). The presence of water in the reaction area may also lead to a hydration of IPAc to form IPol and acetic acid (AAc).

A total of six components were detected in the investigated reaction mixtures using GC-MS, four of which were confirmed using a library search. A comparison of the identified components' spectra with those from the NIST database is presented in Figure 1. The identified components were IPol (NIST# 289584, ID# 19648, DB: mainlib), IPAc (NIST# 429409, ID# 2939, DB: relib), IPEth (NIST# 423843, ID# 4971, DB: relib), and HFBol (NIST# 133587, ID# 1882 DB: mainlib).

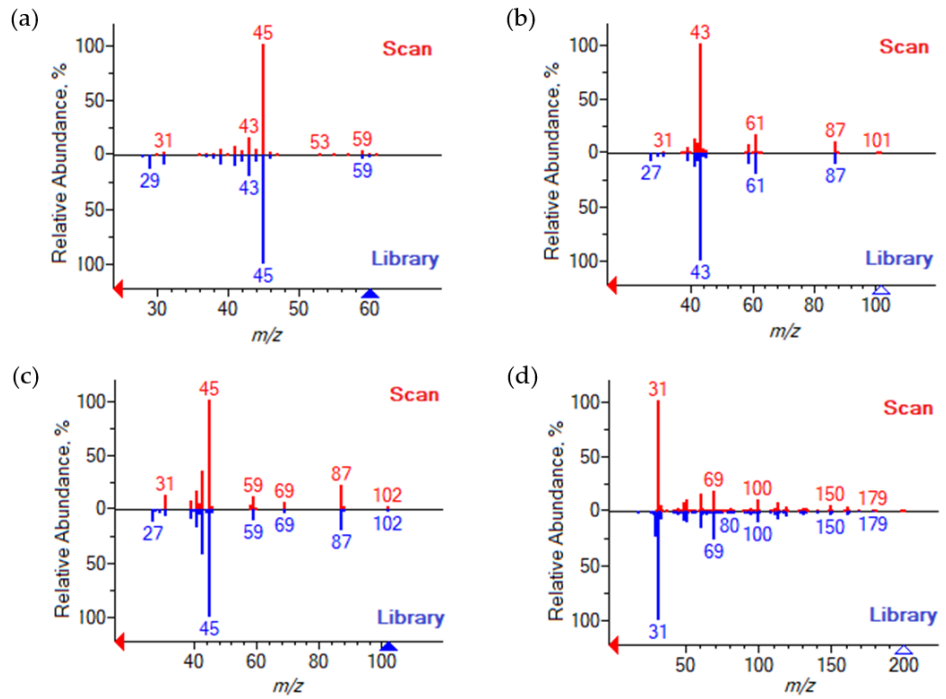


Figure 1. NIST library spectrum matching (red—experimental spectrum; blue—library spectrum): (**a**) Isopropanol; (**b**) Isopropyl acetate; (**c**) Di-isopropyl ether; (**d**) 2,2,3,3,4,4,4-heptafluorobutanol.

The unknown components were identified by fragment ions obtained by electron ionization (EI). Figure 2 presents the mass spectra of these components. In both cases, the heaviest fragment ion is observed at m/z 242. According to the reaction, two products with this molecular mass are possible, HFBAc and HFB-IPEth. The presence of the 2,2,3,3,4,4,4-heptafluorobutyl fragment is evidenced by the occurrence of fragment ions at m/z 69, 119, 169 and 183, which are consistent with chain fragmentation. The observed difference in base ion can be attributed to the preferred fragmentation pathways. In the case of the HFBAc, the preferred fragmentation pathway results in the loss of the acetate group (m/z 43), while in the case of the HFB-IPEth, the methyl group is eliminated, which results in a base ion at m/z 227. Observed EI fragment mass-to-charge ratios and corresponding products ions for HFBAc and HFB-IPEth are listed in Table 2.

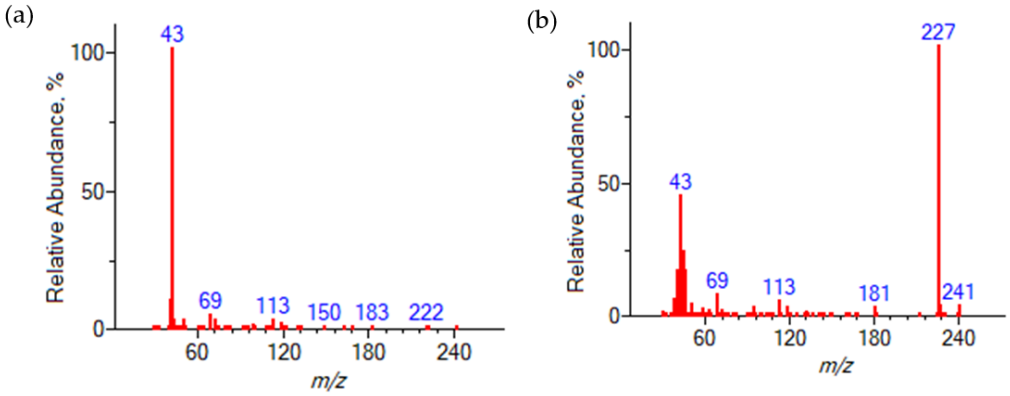


Figure 2. Mass spectra of 2,2,3,3,4,4,4-heptafluorobutyl acetate (**a**) and 2,2,3,3,4,4,4-heptafluorobutyl isopropyl ester (**b**).

Table 2. List of observed EI fragment mass-to-charge ratios and corresponding products ions for heptafluorobutyl acetate (Figure 2a) and 2,2,3,3,4,4,4-heptafluorobutyl isopropyl ester (Figure 2b).

m/*z* (Figure 2a)	Fragment Ion (Figure 2a)	*m*/*z* (Figure 2b)	Fragment Ion (Figure 2b)
242	$[M]^+$	242	$[M]^+$
222	$[M\text{-}HF]^+$	241	$[M\text{-}H]^+$
183	$[CF_3CF_2CF_2CH_2]^+$	227	$[M\text{-}CH_3]^+$
169	$[CF_3CF_2CF_2]^+$	169	$[CF_3CF_2CF_2]^+$
150	$[C_3F_6]^+$	119	$[C_2F_5]^+$
119	$[C_2F_5]^+$	69	$[CF_3]^+$
100	$[C_2F_4]^+$	64	$[CF_2CH_2]^+$
69	$[CF_3]^+$	59	$[i\text{-}PrO]^+$
64	$[CF_2CH_2]^+$	45	$[CH_2CH{=}OH]^+$
43	$[CH_3CO]^+$	43	$[i\text{-}Pr]^+$

The classical method for organic chemists to identify components is NMR spectroscopy. However, due to the congestion and complexity of the resulting spectra, their interpretation can be unnecessarily time-consuming and sometimes simply impossible. By separating components prior to detection, GC-MS is a powerful tool for the analysis of mixtures of volatile and temperature stable organic compounds, both in addition to NMR spectroscopy and individually. The obtained GC-MS data, literature, and theoretical analyses, as well as NMR spectra of samples of a number of supposed reaction products in pure form provided an opportunity to identify the NMR spectra of the reaction mixture and correlate each of the peaks to their corresponding components (Figure 3).

Thus, through a combination of NMR spectroscopy and GC-MS, it was determined that during the reaction of IPAc and HFBol under acidic conditions, the following were primarily formed in the system: target HFBAc and by-product IPol. The following side-products were identified: IPEth, AAc, water, and HFB-IPEth. No bis(1H,1H-heptafluorobutyl) ether traces were identified in the system. The overall reaction can be represented as follows:

$$\mathrm{HFBol} + \mathrm{IPAc} \longleftrightarrow \mathrm{HFBAc} + (\mathrm{HFB} - \mathrm{IPEth}) + \mathrm{IPol} + \mathrm{AAc} + \mathrm{H_2O} + \mathrm{IPEth}$$

Therefore, it can be stated that there is an intermolecular dehydration between IPol and HFBol and intermolecular dehydration between IPol molecules, which leads to the appearance of water, HFB-IPEth, and IPEth in the system. The presence of water and AAc in the system indicates that the IPAc hydration is taking place. The esterification reaction of AAc and HFBol, as well as the hydrolysis of HFBAc, can also be stated with full confidence. Among the less likely reactions are the following: HFBol + IPEth $\longleftrightarrow$ . . .; IPAc + IPol $\longleftrightarrow$ . . .; HFBAc + Ipol $\longleftrightarrow$ . . .; HFBAc + IPEth $\longleftrightarrow$ . . .; HFB-IPEth + Aac $\longleftrightarrow$ . . ..

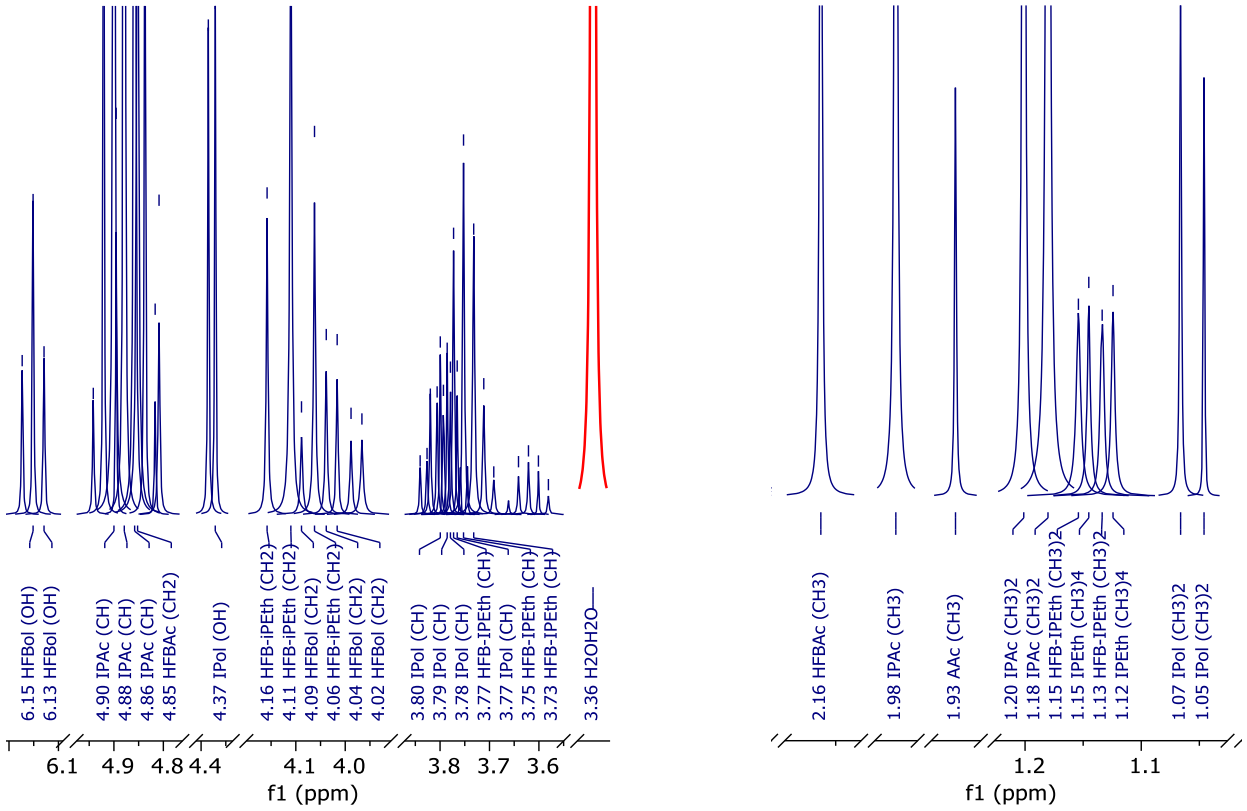


Figure 3. ^{1}H NMR spectrum of the reaction mixture sample in d-DMSO (peak curves). Red line—water peak (identified by the program as partially deuterated).

The data obtained allowed us to correlate atom groups of fluorinated compounds with their chemical shifts on ^{1}H in d-DMSO (Figure 4), ^{19}F, ^{19}F-^{19}F COSY (Figure 5) and ^{13}C{^{19}F} (Figure 6) spectra. The data are summarized in Table 3.

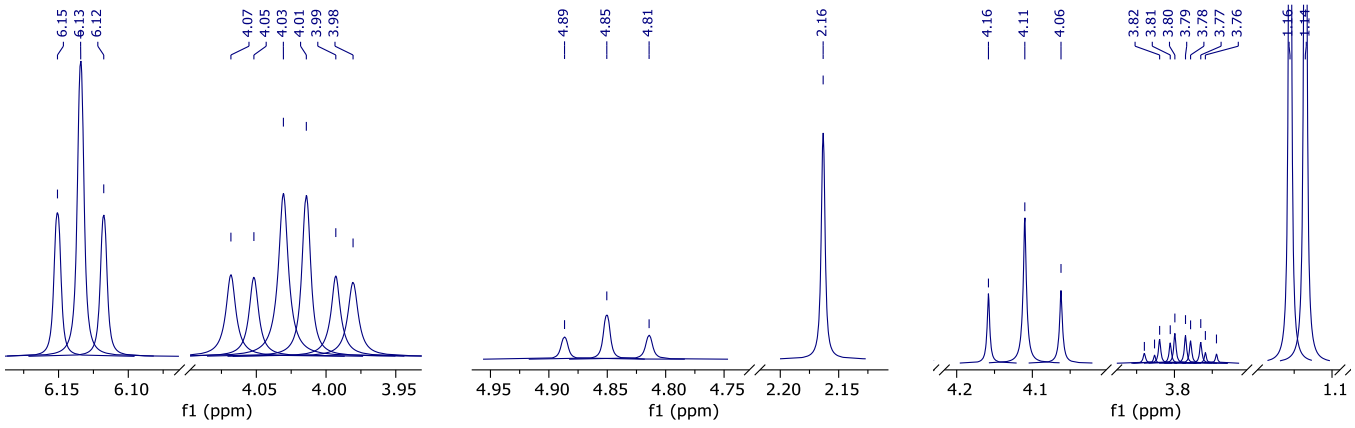


Figure 4. ^{1}H NMR spectrum (peak curves): (**a**)—pure HFBol in d-DMSO; (**b**)—pure HFBAc in d-DMSO; and (**c**)—HFB-iPEth spectrum in d-DMSO isolated from ^{1}H NMR spectrum of the reaction mixture sample.

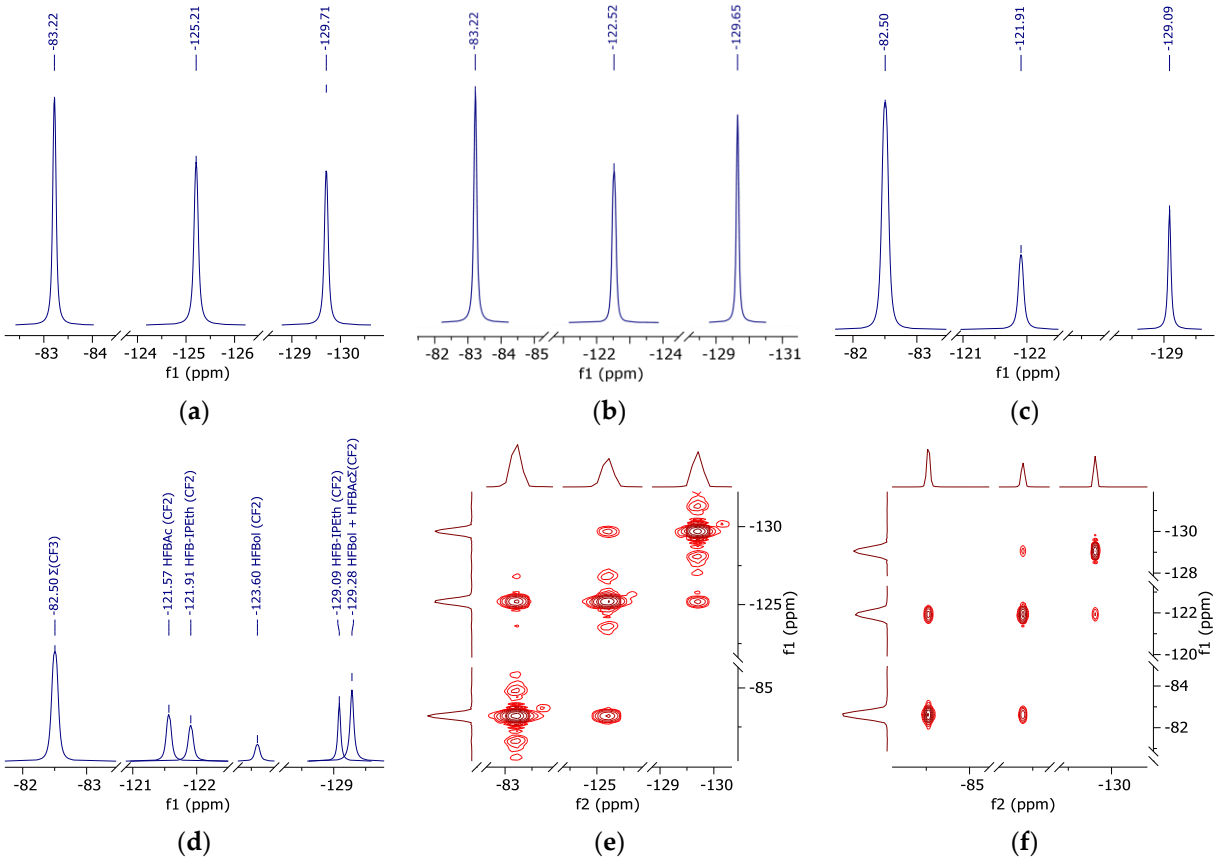


Figure 5. ^{19}F NMR spectrum (peak curves). (**a**)—pure HFBol; (**b**)—pure HFBAc; (**c**)—HFB-iPEth spectrum in d-DMSO isolated from ^{19}F NMR spectrum of the reaction mixture sample; (**d**)—reaction mixture sample in d-DMSO; (**e**)—correlation spectroscopy ^{19}F-^{19}F of HFBol; (**f**)—correlation spectroscopy ^{19}F-^{19}F of HFBAc.

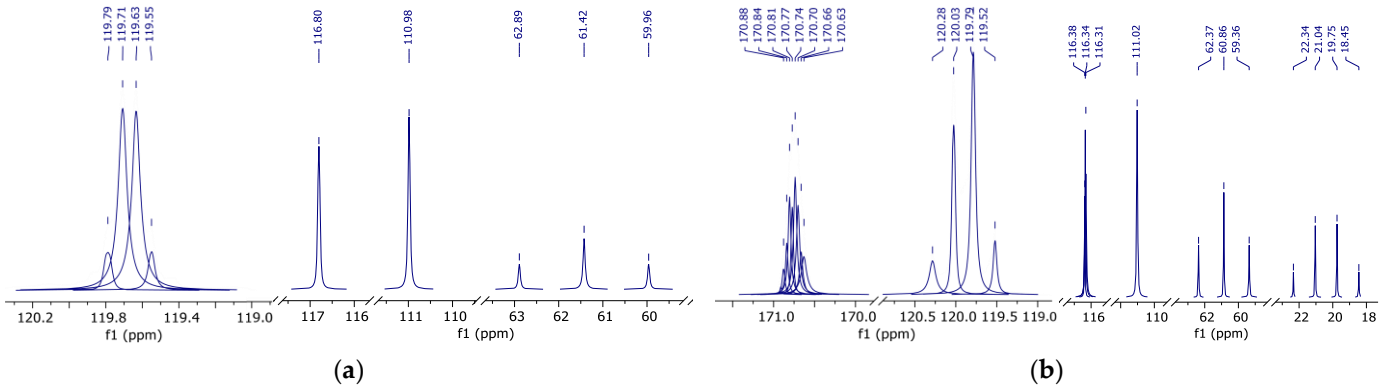
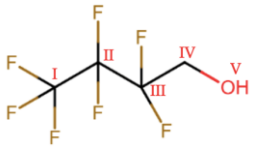
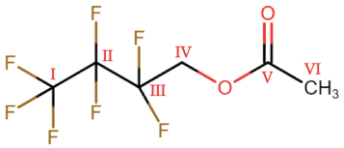
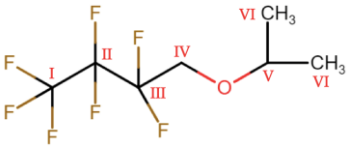


Figure 6. ^{13}C{^{19}F} NMR spectrum with fluorine-19 decoupled (peak curves): (**a**)—pure HFBol; (**b**)—pure HFBAc.

In conclusion, it is worth noting that there is a significant material balance divergence during the RD process for no apparent reason. This can be explained by the formation of propylene during the dehydration of IPol, less likely IPEth. At the same time, the complete dehydration of IPol [18,19] to form water and propylene proceeds under "harsher" conditions compared to those previously investigated. One way or another, propylene formation should be accompanied by the presence of corresponding traces of the component on the ^{1}H NMR spectra of the samples and/or gas emission during the investigation of the

chemical constituent of the process in the stirred reactor. Both conditions were not met in an explicit form.

Table 3. Structure of fluorinated compounds and group chemical shifts.

2,2,3,3,4,4,4-Heptafluorobutanol	2,2,3,3,4,4,4-Heptafluorobutyl Acetate	2,2,3,3,4,4,4-Heptafluorobutyl Isopropyl Ester
		
^{1}H: V 6.13 ppm (t); IV 4.02 ppm (td)—Figure 4a; **^{19}F:** I −83.22 ppm (s); II −125.21 ppm (s); III −129.71 ppm (s)—Figure 5a; **^{13}C{^{19}F}:** III 119.67 ppm (q); II 116.80 ppm (s); I 110.98 ppm (s); IV 61.42÷59.96 ppm (t)—Figure 6a	**^{1}H:** IV 4.85 ppm (t); VI 2.16 ppm (s)—Figure 4b; **^{19}F:** I −83.22 ppm (s); II −122.52 ppm (s); III −129.65 ppm (s)—Figure 5b; **^{13}C{^{19}F}:** V 170.75 ppm (m); III 119.91 ppm (q); II 116.34 ppm (m); I 111.02 ppm (s); V 60.86 ppm (t); VI 19.89 ppm (q)—Figure 6b	**^{1}H:** IV 4.11 ppm (t); V 3.79 ppm (m); VI 1.15 ppm (d)—Figure 4c; **^{19}F:** I −82.50 ppm (s); II −121.91 ppm (s); III −129.09 ppm (s)—Figure 5c

If propylene is formed, it is possible reaction that a reaction could occur in the system between propylene and HFBol, leading to HFB-IPEth formation. The reactions of non-fluorinated olefins with HFBol have not been presented in the literature, but it can be assumed that they proceed similarly to HFBol + hexafluoropropylene interactions. For example, a number of reactions between a type of alcohol with halogen–olefin to form an ether have been discussed in the literature. The reaction of HFBol with hexafluoropropylene is exemplified. This reaction is carried out at 25 °C with 100% conversion, and the content of the target ether in the reaction mixture is 96% [20,21]. Another example is the reaction of HFBol with 3-halagen-1-propene with perfluoroalkyl allyl ether formation [22,23].

4. Conclusions

In the present study, the combination of GC-MS and NMR spectroscopy proved to be an invaluable tool for the successful identification of the components present in the reaction mixture. The approach was used to show and indicate that HFBAc, IPEth, AAc, IPol, water, and HFB-IPEth are formed as the reaction products of IPAc and HFBol. Another important point is that this study provides data on an the new and unstudied compound, HFB-IPEth, for which there was no CAS No. Based on the obtained results, the paper also shows that no bis(1H,1H-heptafluorobutyl) ether traces were identified in the system; the overall reaction and possible interaction among the components of the reaction mixture is described. In addition, original data on the mass spectra and ^{1}H, ^{19}F, ^{19}F-^{19}F COSY and ^{13}C{^{19}F} NMR spectra of the fluorinated compounds are presented. This information is of interest for a wide range of fields of knowledge, where the compounds under study will be addressed in one form or another.

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