A Spectroscopic and Mechanistic Study of the Enolization and Diol Formation of Hexafluoroacetylacetone in the Presence of Water and Alcohol

Sitke Aygen*[a] and Rudi van Eldik[b]

Zentrale Analytik- und Strukturanalyse-Abteilung der Naturwissenschaftlichen Fakultät, Universität Witten/Herdecke[a],
Stockumer Straße 10, D-5810 Witten-Annen (FRG)

Institut für Anorganische Chemie der Universität Witten/Herdecke[b],
Stockumer Straße 10, D-5810 Witten-Annen (FRG)

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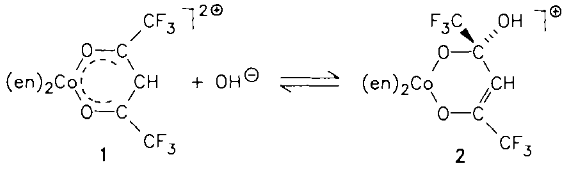
The reactions of hexafluoroacetylacetone (hfac) (**6**) with water, methanol, ethanol, and isopropyl alcohol were studied in detail using ^{1}H-, ^{13}C-, ^{17}O-, ^{19}F-NMR, and UV-VIS spectroscopy. The reported spectra enable the identification of intermediate and product species, and allow a mechanistic analysis of the enolization and diol formation. The suggested mechanisms are discussed with reference to earlier data reported in the literature. An important feature of this study is the direct evidence presented for the formation of the adduct species hfac(OH)$_4$ (**10**), hfac(OMe)$_2$ (**13a**), and hfac(OEt)$_2$ (**13b**).

Eine spektroskopische und mechanistische Untersuchung der Enolisierung und Diol-Bildung von Hexafluoracetylaceton in Gegenwart von Wasser und Alkohol

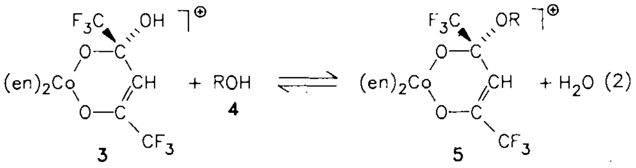
Die Reaktionen von Hexafluoracetylaceton (Hfac) (**6**) mit Wasser, Methanol, Ethanol und Isopropylalkohol wurden im einzelnen anhand von ^{1}H-, ^{13}C-, ^{17}O-, ^{19}F-NMR- und UV-VIS-Spektroskopie untersucht. Dabei konnten die Zwischen- und Reaktionsprodukte bei der Enolisierung und Diol-Bildung spektroskopisch identifiziert werden. Die vorgeschlagenen Reaktionswege werden unter Bezug auf früher in der Literatur berichtete Daten diskutiert. Ein wichtiges Ergebnis dieser Untersuchung ist der direkte Nachweis für die Bildung der Addukt-Spezies Hfac(OH)$_4$ (**10**), Hfac(OMe)$_2$ (**13a**) und Hfac(OEt)$_2$ (**13b**).

The chemical and thermal stability of metal complexes of hexafluoroacetylacetone (hfac) (**6**) has been investigated by various groups[1]. Recently, we reported[2] spectroscopic evidence for the formation of a unique hydrolysis product of coordinated hfac as indicated in (1) and could confirm its structure with the aid of an X-ray diffraction study[3].



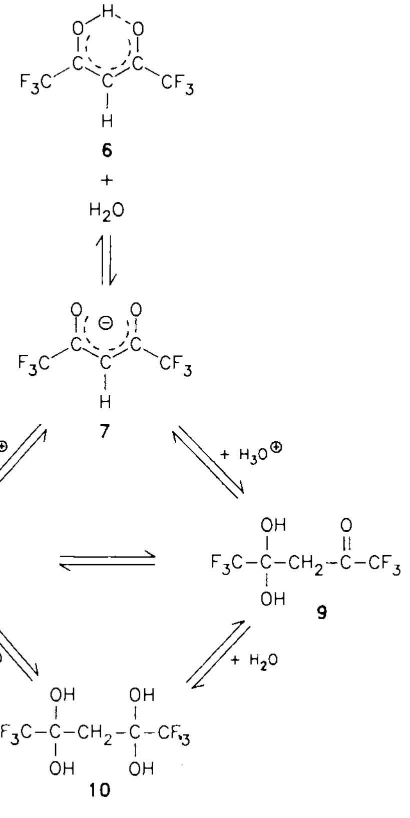
en = ethylenediamine

Subsequent investigations[4] have shown that the hydrolysis product in (1) reacts with different alcohols according to the overall process in (2).



R = Me, Et, *i*Pr

This very interesting behavior of coordinated hfac has motivated us to investigate similar processes for the free, uncoordinated ligand under appropriate conditions. In the pure state or in organic (water-free) solvents, **6** exists to 100% in the enol form[5]. In the presence of water, it rapidly



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hydrolyzes to produce hfac$(OH)_4$ (**10**)[6], which exhibits a series of acid/base equilibria illustrated in (3).

These equilibrium processes strongly depend on the concentration of water and the pH of the medium, as indicated by various investigations[7-10]. The intermediate products **8** and **9** could not be identified spectroscopically up to now since they react relatively fast to **10**. By using a mixture of different solvents (DMSO, DMF, and dioxane) with water, we could control the formation of the species **7** and **9** and identify them using NMR techniques. In addition, we investigated the reaction of hfac with various alcohols and were able to identify similar intermediate steps as those found for water.

The reaction of hfac with H_2O results in the formation of different intermediate species, which exist in acid/base equilibria with each other, before producing the final product **10** as indicated in (3). During the first step, the resonance-stabilized enolate ion **7** is formed[9], and the released protons may catalyze the addition of further water molecules. The ^{19}F-NMR spectrum of hfac in D_2O exhibits a sharp signal for **10** at $\delta = 88.05$ at pH 2.3. An increase in pH to 5−6 (addition of NaOH) resulted in the formation of the enolate ion **7** at $\delta = 77.6$ and some decomposition products (CF_3COCH_3 and CF_3CO_2D with signals at $\delta = 77.8$ and 87.6 ppm, respectively)[9]. When the pure isolated geminal diol is dissolved in an aqueous buffer solution at pH 5, the immediate formation of only a small amount of **7** is observed. No decomposition products, as reported by Duschner et al.[9], were found under these conditions even for reaction times up to 10 days. The equilibrium between **10** and **7** remained unchanged.

The addition of water to DMSO or dioxane enabled a study of the intermediate species **7** and **9** since their formation is significantly slower under such conditions. A ^{19}F-NMR spectrum of hfac in $[D_6]DMSO/D_2O$ (98:2) shows a sharp signal ascribed to **7** at $\delta = 74.4$ (see Table 1), two singlets at $\delta = 83.26$ and 76.15 ascribed to the unsymmetrical CF_3 groups on hemiacetal **9**, and a singlet at $\delta = 84.2$ due to **10**.

The rate of formation of **10** is enhanced as expected on increasing the water concentration and the acidity of the medium. The ^1H-NMR spectrum of hfac in pure $[D_6]$-DMSO exhibits no OH signals, which means that hfac only exists in the enolate form **7** and not in the enol form **6**. The signals at $\delta = 5.20$ and 7.74 are assigned to the protons on CH and H_2O (shifted to lower field in acidic medium). On addition of one drop of H_2O, two additional signals appear at $\delta = 3.2$ and 2.1 and are assigned to the CH_2 group of **10** and **9**, respectively (Table 1). After 10 minutes, the signals due to **7** at $\delta = 5.2$ disappear, and the signal of **10** increases (compare ^{19}F-NMR spectrum in Table 1). It follows that hfac exists only in the enol form in inert solvents such as acetone, whereas the resonance-stabilized enolate ion is favored in water or aqueous solvents such as DMSO and DMF. **7** reacts, depending on the pH and water concentration of the medium, via **9** to **10**. A summary of the ^{19}F-, ^1H-, ^{13}C-, and ^{17}O-NMR data for hfac and its products in acetone, $[D_6]DMSO$, $[D_7]DMF$, D_2O, and $[D_4]$dioxane is given in Table 1.

The slow reverse reaction, i.e. when pure **10** is dissolved in pure $[D_6]DMSO$, $[D_7]DMF$, or $[D_4]$dioxane and produces the enolate ion **7**, can also be followed using ^{19}F- and

Table 1. NMR data of hfac (**6**) and its products in different solvents (δ in ppm, *J* in Hz)

Compound	Solvent	^{19}F NMR	^1H NMR	^{13}C NMR	^{17}O NMR
6	$[D_6]$acetone	75.8	CH: 6.6 OH: 11.85	CO: 173.3 q ($^2J_{CO,F} = 38$) CF_3: 116.5 q ($J_{CF} = 280$) CH: 93.2 s	CO: 278
	$[D_6]Me_2SO$	74.4	CH: 5.24		CO: 384
	$[D_7]DMF$	76.15	CH: 5.5		
	D_2O	88.05 gem. diol	CH_2: 2.04	CO: 94.2 q ($^2J_{CO,F} = 27.2$) CF_3: 112.8 q ($J_{CF} = 279$) CH : 34.0 s	COH: 59 *)
	$[D_4]$dioxane	76.05			
10	$[D_6]$acetone	86.13	CH_2: 2.24 OH : 6.96	CO: 95.8 q ($^2J_{CO,F} = 30.0$) CF_3: 123.7 q ($J_{CF} = 279$) CH : 33.3 s	COH: 61
	$[D_6]Me_2SO$	84.20	CH_2: 3.2		COH: 56
	$[D_7]DMF$	85.90	CH_2 : 2.3		
	D_2O	88.05	CH_2 : 2.4	see hfac	COH: 59
9	$[D_6]$acetone	85.10 73.00	CH : 2.4		
	$[D_6]$ Me_2SO	76.15 83.26	CH_2: 2.1		CO: 589 COH: 56
	$[D_7]DMF$	85.04 77.96	CH_2 : 2.5		
	$[D_4]$dioxane	84.42 73.14			

*) In D_2O compound **10** results from **6**.

^{1}H-NMR techniques. In the case of thoroughly dried [D$_7$]DMF, the stepwise release of water occurs faster. After ca. 30 minutes, an equilibrium between species **7**, **9**, and **10** is reached. The ^{17}O-NMR spectrum of ^{17}O-enriched hfac in [D$_6$]DMSO exhibits three characteristic signals (Figure 1) at δ = 56 (OH groups of **9** and **10**), 384 (CO group of enolate ion **7**), and 589 (CO group of **9**).

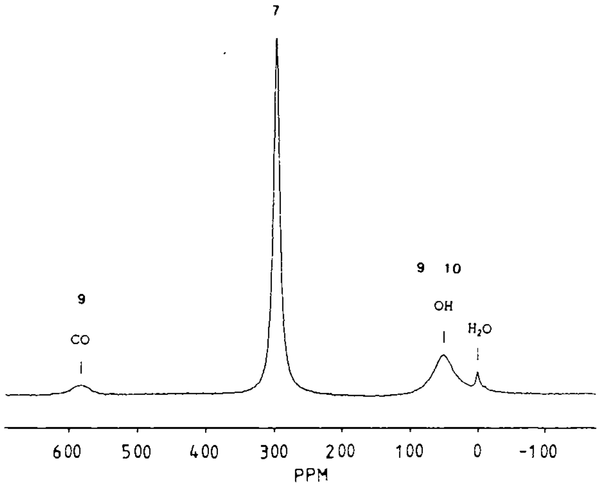
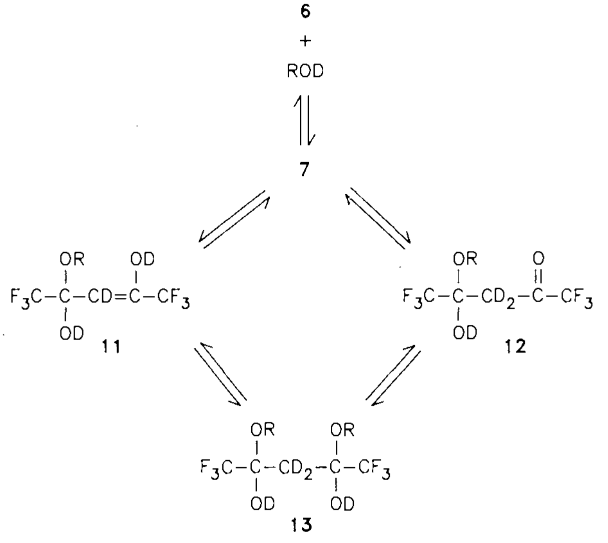


Figure 1. ^{17}O-NMR spectrum of hfac at 40.5 MHz in [D$_6$]DMSO + H_2O

The reactions of hfac with MeOH, EtOH, and *i*PrOH are significantly slower than the reaction with water. The nature of the intermediate and product species can be well characterized with the aid of ^{19}F-NMR. The reaction products of hfac with MeOH and EtOH are discussed in the literature[10]; however, the intermediate steps of these reactions were not characterized unequivocally. The overall reaction scheme for the reaction with CD_3OD can be summarized as shown in (4).



(4)

R = Me, Et, *i*Pr

The spectrum recorded 30 seconds after mixing (Figure 2A) exhibits signals for **7** at δ = 78.3, for the hemiacetal hfac(OCD_3) (**12**) at 75.4 and 86.4, and for the bis(hemiacetal) hfac$(OCD_3)_2$ (**13**) at 83.6 and 83.7.

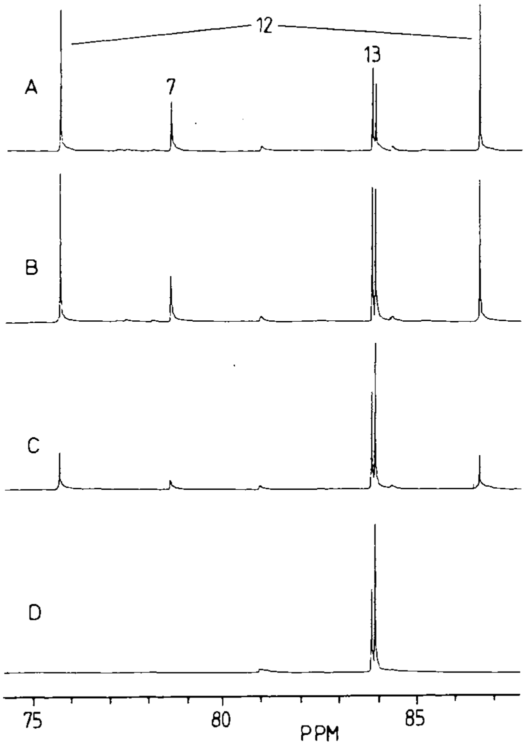
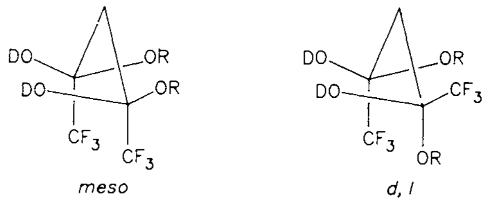


Figure 2. ^{19}F-NMR spectra of hfac in CD_3OD; A) after 30 sec, B) after 90 sec, C) after 10 min, D) after 14 min

The spectra in Figure 2B and 2C, recorded after 90 seconds and 10 minutes clearly indicate that the concentrations of **7** and **12** have decreased significantly, whereas the concentration of **13** has increased almost to the final value reached at complete conversion after 14 minutes. Species **13** exhibits two signals in the ratio of 40:60, which are most likely due to the isomers indicated in (5).



(5)

This isomeric ratio remains constant over long periods of time, and no evidence for any decomposition products was obtained.

The same system was investigated with the help of ^{13}C-NMR techniques (Table 2).

Two quadruplets of different intensity for the CF_3 groups at δ = 123.7 and 124.3 [J(CF) = 298.3 Hz] and two overlapping quadruplets of weak intensity (due to NOE effect) for the neighboring CF_3 carbon atoms between δ = 97 and 99. In addition, the CD_2 group exhibits two triplets at δ = 36.5 and 35.7 [J(CD) = 19.8 Hz] for which the expected intensity ratio of 1:1:1 is affected by the incomplete deu-

Table 2. NMR data of hfac (**6**) and ist product species in alcohols (δ in ppm, *J* in Hz)

Compound	Solvent	^{19}F NMR	^{1}H NMR	^{13}C NMR
6	CH_3OD	77.0, 88.1 hemiacetal 79.9 enolate 85.3, 85.5 bis-hemiacetal ($^4J_{FH}$= 1.5)	-	2CO: ca. 96-98.0 q, CF_3(I): 122.8 q, CF_3(II): 123.4 q (J_{CF}= 289.0) CH_2(I): 35.2, CH_2(II): 36.1, OCH_3(I): 49.7, OCH_3(II): 50.2 CH_3OD: 49
	CD_3OD	75.4, 86.4 hemiacetal 78.3 enolate 83.6, 83.8 bis-hemiacetal	-	2CO: 97-99.0 q, CF_3(I): 123.7 q, CF_3(II): 124.3 q (J_{CF}= 289.3) CD_2(I): 36.5 f, CD_2(II): 35.7 t (J_{CD}= 19.8), 2OCD_3: ca. 52. CD_3OD: 51
hfac$(OCH_3)_2$	[D_6]acetone	81.3 q ($^4J_{FH}$ = 1.4)	CH_2: 2.28 CH_3: 3.53 q ($^4J_{HF}$= 1.4) OH: 6.19	CO: ca. 97.5 q, CF_3: 123.5 (J_{CF} = 284.3), CH_2: 35.8 OCH_3: 51.2
6	C_2H_5OD	77.3, 88.3 hemiacetal 80.2 enolate	-	CO(I): 97 q ($^2J_{CF}$= 31.2) CO(II,III): ca. 94-96 one of hfac$(OH)_4$, CF_3(I): 122.1 (J_{CF}= 289)
		85.13, 85.7, 85.83 bis-hemiacetal		CF_3(II): 123.0, CF_3(III): 122.7 (hfac$(OH)_4$), CH_2(I,II,III): 40.3, 35.6, 34 OCH_2(I,II): 59.2, 58.3, CH_3(I,II,III): 15.1, 14.5, 14.47
	C_2D_5OD	75.25, 86.2 hemiacetal 78.1 enolate 83.12, 83,68, 83.77 bis-hemiacetal	-	CO(I): 98.1 q ($^2J_{CF}$= 31.6), CO(II,III): ca. 95-97, CF_3(I): 123.2 (J_{CF}= 289) CF_3(II,III): 124.2, ca. 123, OCD_2(I,II,III): 59.63, CD_2(I,II,III): 41.74, 37.28, 35.7, CD_3(I,II,III): 14.88 CD_3CD_2OD: 17.20, 57.3
hfac$(OEt)_2$	[D_6]acetone	81.58	CH_2(I): 4.08 q of d $^2J_{H,H}$= 7.14, ($^2J_{H,H}$ = 9.7) CH_2(II): 3.74 q of q of d ($^4J_{H,F}$ = 1.4) CH_2: 2.3 s CH_3: 1.23 t OH: 6.2	CO: ca. 97 q, CF_3: 123 q (J_{CF} = 289.7) OCH_2: 60.1 s, CH_2: 35.1 s, CH_3: 15.89
6	iso-C_3D_7OD	77.4, 87.85 hemiacetal 80.2 enolate 82.3, 84.6, 85.4, 85.9 bis-hemiacetal		

teration of the CH_2 moiety. The OCD_3 carbons are observed as septuplets next to free CD_3OD at $\delta \approx 51$. The strong overlap between the OCD_3 and CD_3OD signals prohibits an unequivocal assignment. In order to improve the assignment of these signals, the reaction was repeated with CH_3OD (Figure 3).

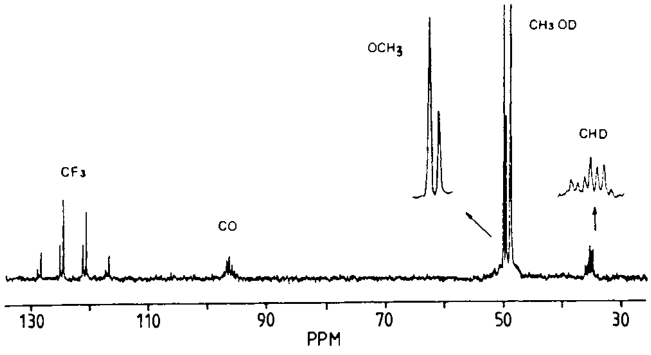


Figure 3. $^{13}C\{^1H\}$-NMR spectrum of hfac in CH_3OD

Two singlets are now observed for the OCH_3 carbons at $\delta = 49.7$ and 50.2 and a signal for free CH_3OD at $\delta = 49$. The ^{19}F-NMR spectrum of hfac in CH_3OD exhibits two quadruplets at $\delta = 85.3$ and 85.5 [^4J(FH) ≈ 1.5 Hz] compared to two singlets at $\delta = 83.6$ and 83.8 in CD_3OD. The isomeric ratios of *meso*:*d,l* are similar in both cases (Table 2).

Colorless crystals of hfac$(OCH_3)_2$ could be isolated from a slow evaporation of CH_3OD in an N_2 atmosphere. The ^{19}F-NMR spectrum of this compound dissolved in [D_6]acetone exhibits a quadruplet at $\delta = 81.3$ [^4J(CF) = 1.4 Hz] (Table 2). The ^{1}H-NMR spectrum of this solution exhibits resonances at $\delta = 2.28$ (s, CH_2), 3.53 [q, ^4J(HF) = 1.4 Hz, CH_3], and 6.19 (OH) (Table 2). The $^{13}C\{^1H\}$-NMR spectrum indicates resonances at $\delta = 123.5$ [q, ^1J(CF) = 284.3 Hz, CF_3], 97–98 (weak q, F_3C-C^*-OD, due to NOE), 51.2 (sharp s, OCH_3), and 35.8 (s, CH_2, split due to incomplete deuteration) (Table 2). All the recorded ^{1}H-, ^{19}F-, and ^{13}C-NMR spectra of the isolated hfac$(OCH_3)_2$ indicate unequivocally that no isomers are produced in acetone. The reaction of hfac in MeOH was also studied by UV spectroscopy following the characteristic absorption of the enolate form **7** at $\lambda = 302$ nm as a function of time. To study the reaction of hfac with ethanol, a 20% solution in C_2H_5OD was prepared. Four different reaction products could be identified by ^{19}F-NMR 30 seconds after mixing: the enolate form **7** at $\delta = 78.1$, hemiacetal hfac(OC_2H_5) (**11**) at $\delta = 75.25$ and 86.4 (similar intensity), bis(hemiacetal) hfac$(OC_2H_5)_2$ (**13**) at $\delta = 83.12$, 83.68, and 83.77 (different intensity), and a signal for hfac$(OD)_4$ at $\delta = 88.6$ (due to the presence of some water in alcohol) (Figure 4).

The formation of the intermediate species is similar to that reported for the reaction with methanol, but the reactions are significantly slower in the case of ethanol with a

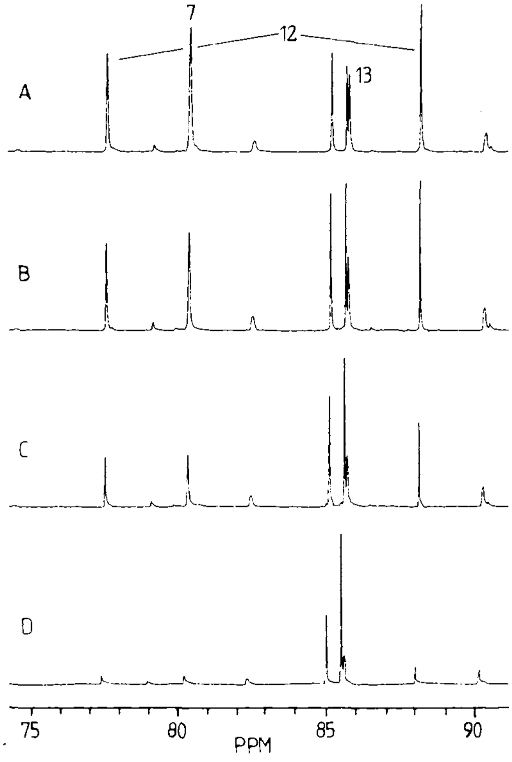


Figure 4. ^{19}F-NMR spectra of hfac in C_2D_5OD; A) after 30 sec, B) after 5 min, C) after 12 min, D) after 50 min

total reaction time of 50 minutes. For the formation of bis(hemiacetal) **13**, three isomers are observed (compare CH_3OD). The ratio of these isomers in CH_3OD and C_2H_5OD remains unchanged over a longer period of time (up to 6 weeks). The sample was investigated by ^{13}C NMR (see Figure 5) showing three quadruplets of different intensity at $\delta = 122.2$ (strongest), 123.0, and 122.7 [$J(CF) = 288.8$ Hz] for the CF_3 groups, three quadruplets for the F_3C-C^*-OD group, one at $\delta = 98.1$ [$^2J(CF) = 31.2$ Hz] (strongest), and two of weaker intensity overlapping between $\delta = 95-97$.

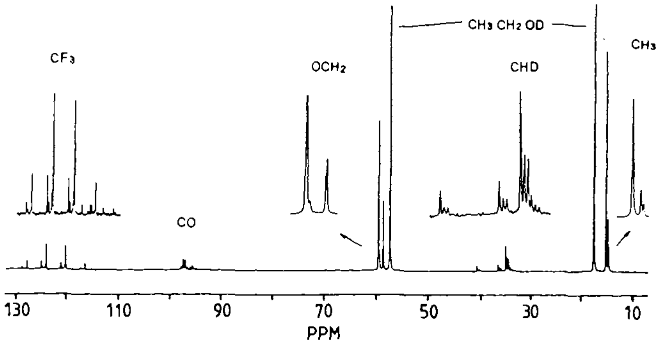


Figure 5. $^{13}C\{^1H\}$-NMR spectrum of hfac in C_2H_5OD

In both cases, the third quadruplet of weaker intensity is due to the side product hfac$(OH)_4$. In addition, there are two separated singlets for $OC^*H_2-CH_3$ at $\delta = 59.2$ and 58.3, three singlets at $\delta = 40.3$, 35.6, and 34.6 that are split due to incomplete deuteration of the CH_2 groups, and three singlets for $OCH_2-C^*H_3$ at $\delta = 15.1$, 14.5, and 14.47 (Figure 5).

Slow evaporation of EtOH in an N_2 atmosphere results in the formation of colorless crystals of hfac$(OEt)_2$. The ^{19}F-NMR spectrum in [D_6]acetone exhibits signals at $\delta = 81.58$ and 86.4, of which the latter is due to the byproduct hfac$(OH)_4$ (Table 2). The ^1H-NMR spectrum of this solution (Figure 6) exhibits a singlet at $\delta = 6.99$ for OH in hfac$(OH)_4$, a singlet at $\delta = 6.2$ for OH in hfac$(OEt)_2$, a quadruplet of doublets at $\delta = 4.08$ for the CH_2(I) group in OEt [$^2J(HH) = 9.7$, $^2J(HH) = 7.14$ Hz], and a quadruplet of quadruplets of doublets for the other CH_2(II) group of OEt at $\delta = 3.74$ since they are bound to unsymmetrical carbon atoms.

In the latter case each quadruplet is split into a further quadruplet due to fluorine coupling [$^4J(HF) = 1.44$ Hz]. The spectrum (Figure 6A) also shows a quadruplet and triplet for free C_2H_5OH at $\delta = 3.56$ and 1.11, respectively, CH_2 resonances at $\delta = 2.3$ and 2.2 due to hfac$(OEt)_2$ and

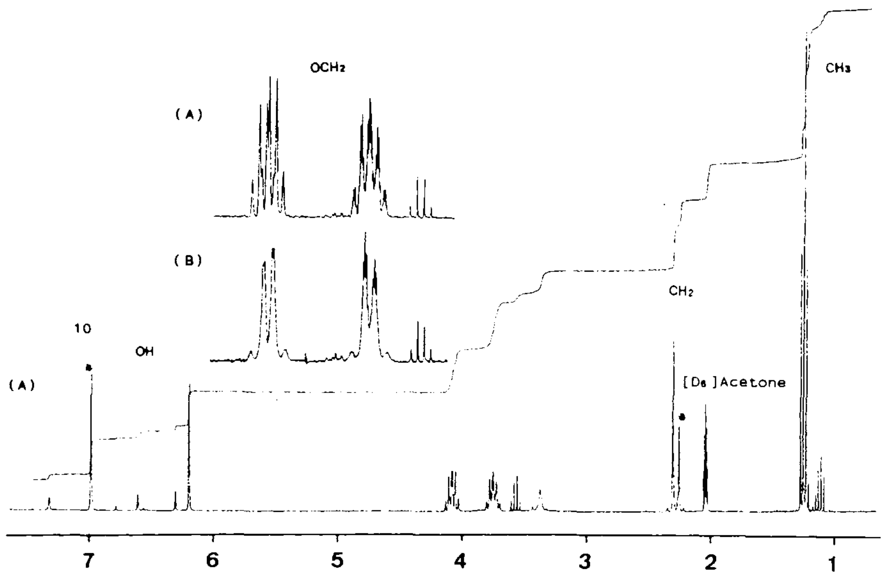


Figure 6. ^1H-NMR spectra of isolated hfac$(OEt)_2$ at 300 MHz in [D_6]acetone (A), CH_3-decoupled (B)

hfac(OH)$_4$, and a triplet at $\delta = 1.23$ due to the coordinated $OCH_2^*CH_3$ [$^2J(HH) = 7.14$ Hz]. Through selective decoupling of CH_3 in the OEt groups the spectrum could be simplified significantly (Figure 6B). At $\delta = 4.08$ and 3.74 it exhibits doublets for CH_2(I) and CH_2(II) groups, respectively, where one of the CH_2 quadruplet signals is split through HF coupling [$^4J(HF) = 1.4$ Hz] (Figure 6B).

The ^{13}C-NMR spectrum of this solution exhibits a quadruplet at $\delta = 123$ for the CF_3 groups [$J(CF) = 289.7$ Hz], a quadruplet of weak intensity (due to NOE effect) for $EtO-C^*-OD$ at $\delta = 94.8$, a sharp singlet for $^*CH_2CH_3$ groups at $\delta = 60.06$ and, a singlet for $CH_2-C^*H_3$ groups of hfac(OEt)$_2$ at $\delta = 15.83$ (Table 2). These ^1H-, ^{19}F-, and ^{13}C-NMR spectra of the isolated hfac(OEt)$_2$ dissolved in [D$_6$]acetone unequivocally indicate no isomers. The reaction of hfac with EtOH could also be followed spectrophotometrically by following the absorption maximum at $\lambda = 269$ nm.

The reaction of hfac with [D$_8$]isopropyl alcohol was also studied using ^{19}F NMR. The following products could be observed after 30 seconds: the enolate form **7** at $\delta = 80.2$ and hemiacetal hfac(*i*PrOH) (**12**) at $\delta = 77.4$ and 87.85 (Table 2). After ca. 15 minutes further signals of different intensity appear at $\delta = 82.3$, 84.6, 85.4, and 85.9 that most probably belong to **13** (Table 2). This reaction occurs even slower than in EtOH and requires 210 minutes for completion. Slow evaporation of *i*PrOH in N_2 atmosphere did not lead to the isolation of a product.

Experimental

NMR spectra were recorded on Varian XL 100 and Bruker AM 300 spectrometers. UV-VIS spectra were recorded on a Perkin-Elmer 555 spectrophotometer equipped with a thermostated (± 0.1°C) cell compartment, which was also used in some preliminary kinetic measurements.

Hexafluoroacetylacetone (Aldrich, bp 69°C) was purified by double distillation. Hfac(OH)$_4$ was prepared as described in the literature[6], washed with benzene, dried in vacuum for 2 h, and stored in an N_2 atmosphere. Hfac(OCH$_3$)$_2$ and hfac(OC$_2$H$_5$)$_2$ were prepared[8] by the slow evaporation of mixtures of hfac and MeOH and EtOH, respectively, in an N_2 atmosphere. The products were washed with benzene and dried in vacuum.

CAS Registry Numbers

6: 1522-22-1 / **9**: 117960-69-7 / **10**: 428-75-1 / **13a**: 117960-67-5 / **13b**: 117960-68-6 / MeOH: 67-56-1 / EtOH: 64-17-5 / *i*PrOH: 67-63-0

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