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Deoxyfluorination with superacids – synthesis and characterization of protonated α -fluorohydroxyacetic acid†

 Alan Virmani,[‡] Christoph Jessen, Alexander Nitzer and Andreas J. Kornath[‡]

α -Fluoroalcohols describe a rare and unstable class of compounds, accessible mainly by fluorination of highly electrophilic carbonyl compounds. In this work, we report the syntheses of α -fluorohydroxyacetic acid (FHA) and its acyl fluoride (FHA-F) by reacting the dihydroxy species glyoxylic acid monohydrate (GAM) with SF₄. Surprisingly, only one of the geminal hydroxy groups is substituted when excess SF₄ is employed. Implementing GAM with the binary superacid HF/AsF₅ also leads to a single yet quantitative deoxyfluorination at the diol group. The reaction pathways are discussed based on NMR experiments, the characterization was carried out using NMR and vibrational spectroscopy as well as single-crystal X-ray diffraction.

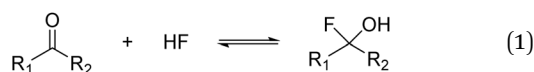
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Introduction

Organic compounds containing carbon atoms with more than one hydroxy group are known to be labile under regular conditions. According to the rule of Erlenmeyer, they undergo facile dehydration under the formation of the respective carbonyl compound. This also applies to alcohols with a geminal halogen atom, where the hydrogen halide is easily eliminated.¹ In the case of fluorinated compounds, only a few examples of α -fluoroalcohols are known. Fluoromethanol CFH₂OH, the simplest representative, was synthesized by Olah and Pavláth as early as 1953.² In 1977, Seppelt was able to generate the perfluorinated alcohol trifluoromethanol CF₃OH by reacting CF₃OCl with HCl. He operated at low temperatures to prevent the decomposition under the formation of COF₂ and HF, which is highly favored.³ 30 years later, Christie *et al.* investigated this equilibrium.⁴ The addition of HF or F⁻ to a carbonyl group is a convenient way to access (per-)fluorinated alcohols, first shown by Andreasdes and England in 1961,⁵ followed by others in recent studies.^{6,7} The general equation is given below (eqn (1)).



However, the α -fluoroalcohol is only stable when the electrophilicity of the carbonyl group is high enough, similar to the rule of Erlenmeyer.⁸ The equilibrium of eqn (1) can be shifted to the right by transforming the alcohol into stable derivatives like acetals or oxonium ions.^{4,9,10} The respective oxonium ions were generated by reacting the carbonyl compounds with the superacidic system HF/SbF₅ in anhydrous hydrogen fluoride (aHF). In this way, the perfluorinated oxonium ions of methanol, ethanol, *n*-propanol,¹⁰ and isopropanol¹¹ have been synthesized.

An example of an exception to the rule of Erlenmeyer is glyoxylic acid (GA). The purchasable monohydrate form (GAM) does not imply co-crystallized but chemically bound water and is better described as dihydroxyacetic acid. Its reactivity toward highly acidic systems, in which it can be activated for electrophilic reactions, has been described by Prakash *et al.*¹² The high electrophilicity makes it an interesting target for generating α -fluorohydroxy compounds with an additional functional group in the direct vicinity. To exploit this possibility or to determine if a difluorinated product is formed, we have implemented GAM with the deoxyfluorinating agent SF₄ as well as the superacidic medium HF/AsF₅. We wish to report the results herein.

Results and discussion

Syntheses and properties

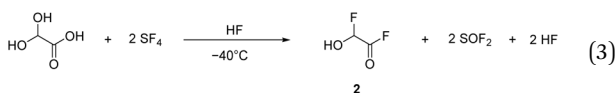
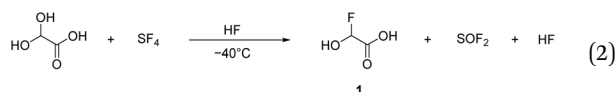
α -Fluorohydroxyacetic acid (FHA, **1**) is synthesized by reacting glyoxylic acid monohydrate (GAM) with an equimolar amount of sulfur tetrafluoride (eqn (2)). For the synthesis of α -fluorohydroxyacetyl fluoride (FHA-F, **2**), a twofold amount of SF₄ is applied (eqn (3)). The formation of difluoroacetyl fluoride was not observed with an excess of SF₄.

Ludwig-Maximilians-Universität München, Butenandtstraße 5-13 (D), D-81377 München, Germany

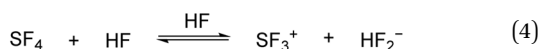
† Electronic supplementary information (ESI) available: For full details on vibrational spectroscopy, NMR spectroscopy, X-ray diffraction refinement, and computational details. CCDC 2173682. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4ra05449k>

‡ Prof. Kornath passed away in March 2024.





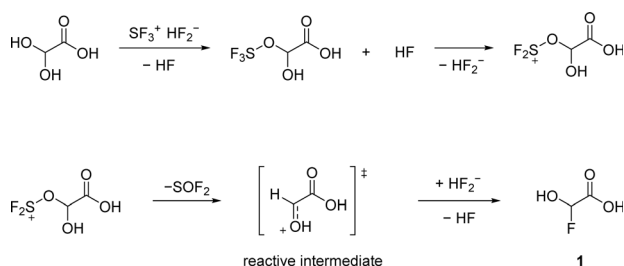
The mechanism of GAM in the system HF/SF₄ is proposed based on the literature-reported pathways of similar reactions.^{13–15} In the first step, SF₄ dissociates in aHF according to eqn (4).



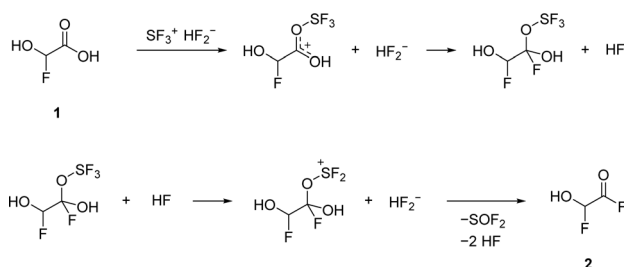
We confirm that the alcohol moiety is more nucleophilic than the carboxy group, which is why the first deoxyfluorination takes place there (Scheme 1). The reactive intermediate is a planar oxonium ion. Since the addition of a nucleophile in this mechanism is not stereoselective, a racemic mixture is expected.

The second deoxyfluorination of the carboxylic group proceeds in a similar fashion. However, in this case, the formation of a tetrahedral intermediate is likely, as it has been suggested in previous studies about the reactions of carbonyl compounds with HF/SF₄.^{13,15} The proposed mechanism is illustrated in Scheme 2.

Employing three or more equivalents of SF₄ did not result in a third deoxyfluorination of the last hydroxy group, hence in 2,2-



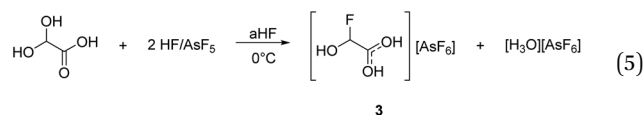
Scheme 1 Proposed reaction pathway of GAM with equimolar amounts of SF₄.



Scheme 2 Proposed reaction pathway of the deoxyfluorination reaction at the carboxy group.

difluoroacetyl fluoride. Since the cationic intermediate would be a fluoro carbenium ion, it is presumably not sufficiently stabilized.

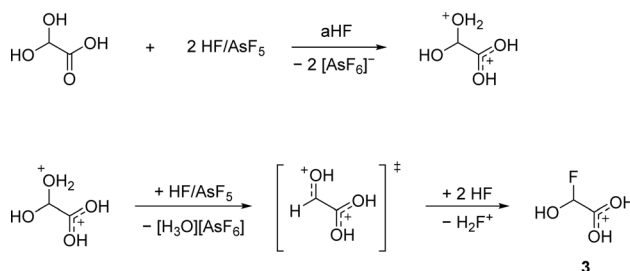
The deoxyfluorination agent SF₄ has been investigated in the past.^{13,15} Interestingly, a similar reaction is observed for GAM reacting with superacids. Protonated α-fluorohydroxyacetic acid [FHA-1H]⁺ is generated from GAM in the superacidic system HF/AsF₅, resulting in [FHA-1H][AsF₆] (3). The reaction is visualized in eqn (5).



According to eqn (5), a two-to-one ratio of AsF₅ to GAM would formally suffice to form [FHA-1H][AsF₆]. However, full conversion takes place only when three equivalents of Lewis acid are applied. The carboxy group is more basic than the hydroxy groups due to better resonance stabilization, which is why it is likely protonated in the first step. The second protonation occurs at one of the hydroxy groups that subsequently is eliminated as H₃O⁺. The formed substituted ethylene dication [C₂(OH)₃H]²⁺ is superelectrophilic enough to add fluoride from the solvent aHF, similar to observations we made in a recent study.¹⁶ 3 is found as a racemic mixture of the two enantiomers, strongly indicating an S_N1 mechanism. The proposed mechanism is displayed in Scheme 3.

The necessity of three equivalents of Lewis acid to form 3 leads to the conclusion that a superelectrophilic carbocation is formed as the reactive intermediate.

Prakash *et al.*¹² showed that the carbonyl group (or dihydroxy group, respectively) of glyoxylic acid can be activated with strong acids in the presence of aromatic compounds for electrophilic reactions to synthesize diarylacetic acid derivatives (eqn (6)). α-Fluorohydroxyacetic acid may be useful similarly to generate aryl-fluoroacetyl acid derivatives (eqn (7)), while α-fluorohydroxyacetyl fluoride has the potential to be activated with Lewis acids at the C1-atom for Friedel-Crafts-acylations (eqn (8)). However, for this kind of reaction, the protonated species of α-fluorohydroxyacetic acid might be a better fit since the carboxy group is already activated and its [AsF₆][−] salt is relatively stable (eqn (9)).



Scheme 3 Proposed mechanism of the synthesis of [FHA-1H]⁺ from GAM.



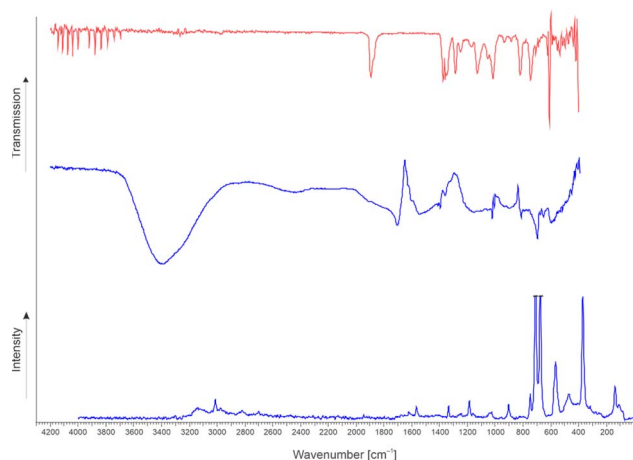


Fig. 1 The infrared spectrum of gaseous **2** at room temperature (top, red). Low-temperature infrared (middle) and Raman spectrum (bottom) of **3** (blue).

C. The sample was warmed up to 0 °C and an infrared spectrum of the gas phase was measured at room temperature. In the case of $[\text{FHA-1H}]^+$, the $[\text{AsF}_6]^-$ salt (**3**) was synthesized by reacting GAM with HF/AsF₅ in aHF and successively removing the solvent *in vacuo* at −78 °C. Infrared and Raman spectroscopy of the colorless residue was performed at low temperatures (see ESI† for more details). The spectra are displayed in Fig. 1 and selected observed frequencies are listed in Table 2. Quantum chemical calculations of the respective compounds were performed to support the assignment of the vibrational frequencies. The detailed characterization of the compounds is found in the ESI.† FHA (**1**) could not be isolated from aHF, so an experimental frequency analysis was not feasible. However, the quantum chemically calculated frequencies and their assignment are listed in Table S3 in the ESI.†

The infrared spectrum of **2** shows rotational bands of remaining hydrogen fluoride between 3728 and 4143 cm^{−1}, which was not completely removed after the reaction. The $\nu(\text{C}=\text{O})$ vibration is observed at 1894 cm^{−1}. This band is distinct for acyl fluorides^{20–22} and is significantly blue-shifted compared to GAM (1742 cm^{−1}).²³ The stretching vibrations of the newly formed CF bonds occur at 1173 (acyl fluoride moiety) and 1016 cm^{−1} (fluorohydroxy group). The intensive bands down

Table 2 Selected observed vibrational frequencies [cm^{−1}] of **2** and **3**

FHA-F	$[\text{FHA-1H}][\text{AsF}_6]$		Assignment
Exp. IR ^a	Exp. IR ^a	Exp. Ra ^b	
1894 (m)	1705 (m)	1567 (7)	$\nu(\text{CO}_a)$
	1541 (m)		$\nu(\text{CO}_a)$
1173 (m)			$\nu(\text{C}(\text{O})\text{F})$
1128 (m)	1151 (m)	1162 (3)	$\nu(\text{C}-\text{OH})$
1016 (m)	1022 (m)	1027 (4)	$\nu(\text{CF})$
822 (m)	897 (m)	903 (8)	$\nu(\text{CC})$

^a Abbreviations: m = medium, a = acid. ^b Experimental Raman intensities are relative to a scale of 1 to 100.

from 708 cm^{−1} are assigned to residual SF₄, which has been observed in the NMR study as well. A reference spectrum of SF₄ is illustrated in Fig. S18 in the ESI.†

In the IR spectrum of **3**, a strong and broad band with a maximum at 3406 cm^{−1} is found. This might be assigned to H₃O⁺, however, it cannot be excluded that this band is attributed to the measurement method at low temperatures, where water can condense onto the specimen, superposing the OH and CH stretching vibrations. The protonation of the carboxy group can be traced by the $\nu_{\text{as}}(\text{CO})$ band at 1705 cm^{−1} (IR), which is red-shifted compared to $\nu(\text{C}=\text{O})$ of GAM (1742 cm^{−1}).²³ The antisymmetric CO stretching mode of **3** occurs at 1541 (IR) and 1567 cm^{−1} and is in return blue-shifted concerning $\nu(\text{C}-\text{O})$ of GAM (1101 cm^{−1}). This convergence of the carboxylic vibrations is a direct result of protonation and has been described in several studies.^{24,25} The stretching vibration of the newly formed CF bond is observed at 1022 (IR) and 1027 cm^{−1} (Ra), similar to **2**.

Crystal structure of $[\text{FHA-1H}][\text{AsF}_6]$

Single crystals of **3** were obtained by dissolving the colorless powder in aHF at −55 °C. Colorless needles suitable for single-crystal X-ray diffraction grew as racemic twins within three days. In the following, the S-enantiomer is discussed. **3** crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units per unit cell. The asymmetric unit is displayed in Fig. 2. Table 3 contains selected geometric parameters.

The C1–C2 bond of 1.515(5) Å is similar to the starting material glyoxylic acid monohydrate (GAM, 1.522(3) Å),²⁶ yet slightly longer than a regular Csp³–Csp² single bond (1.502 Å) in carboxylic acids.²⁷ The C1–O1 (1.258(4) Å) and C1–O2 (1.272(4) Å) bond distances are approximately the same, as has been observed in a variety of protonated carboxylic acids.^{24,25,28} The C2–O3 bond (1.355(5) Å) is significantly shorter than the two C–OH bonds in GAM (1.400(4) and 1.404(3) Å) and even more significant than a regular C–O single bond in primary alcohols (1.426 Å).²⁷ The newly formed C2–F1 of 1.376(5) Å, on the other hand, is longer than a regular C–F bond with an electron-withdrawing group in the geminal position (1.349 Å).²⁷ The nature of this bond relation will be discussed below in the Theoretical Study.

The O1–C1–O2 angle of 120.6(3)° is significantly smaller than in GAM (125.1(2)°)²⁶ as a result of the protonated carboxy group. Subsequently, the O1–C1–C2 is widened from 111.9(2)°

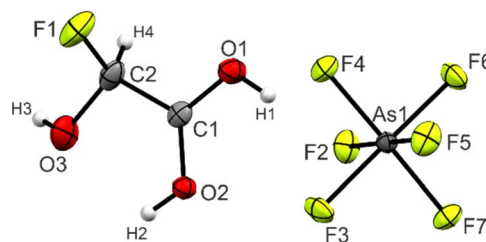


Fig. 2 Projection of the asymmetric unit of **3** (50% probability displacement ellipsoids, hydrogen atoms displayed as spheres of arbitrary radius).



Table 3 Selected geometric parameters of **3**. Symmetry codes: $i = x, 1 + y, z$; $ii = 1.5 - x, 2 - y, 0.5 + z$

Bond lengths [Å]		Intermolecular interactions D(-H)⋯A [Å]	
C1–O1	1.258(4)	O1(-H1)⋯F2	2.579(4)
C1–O2	1.272(4)	O2(-H2)⋯O3	2.587(4)
C1–C2	1.515(5)	O2(-H2)⋯F6 <i>i</i>	2.669(3)
C2–O3	1.355(5)	O3(-H3)⋯F3 <i>ii</i>	2.826(4)
C2–F1	1.376(5)	C1⋯F7	2.733(5)

Bond angles [deg]		Dihedral angles [deg]	
O1–C1–O2	120.6(3)	O3–C2–C1–O1	179.5(4)
O1–C1–C2	117.4(3)	F1–C2–C1–O1	−61.2(5)
O2–C1–C2	122.0(3)	O3–C2–C1–O2	−1.0(6)
O3–C2–C1	106.6(3)	F1–C2–C1–O2	118.3(4)
F1–C2–C1	106.1(4)		
O3–C2–F1	111.9(4)		

in **GAM** to 117.4(3)° in **3**, while the remaining bond angles remain approximately unchanged. Regarding the torsion angles, the O3–C2–C1–O2 dihedral is reduced from 9.9(9)° to −1.0(6)°. This is due to an intramolecular hydrogen bond O2(−H2)⋯O3 with a distance of 2.587(4) Å that is formed upon protonation. The cation exhibits three additional, moderately strong hydrogen bonds²⁹ (Fig. 3) to form layers in the *bc*-plane (O1(−H1)⋯F2, O2(−H2)⋯F6, and O3(−H3)⋯F3). These layers are connected along the *a*-axis by nearly perpendicular C1⋯F7 interactions with a distance of 2.733(5) Å (Fig. S21, ESI†), which is about 14% within the sum of the van-der-Waals radii (3.17 Å).³⁰

The bond distances of the anion range between 1.698(3) and 1.754(2) Å. As–F bonds involved in donor–acceptor interactions (As1–F2, As1–F6, and As1–F6) are slightly longer than the others, resulting in a distorted octahedral structure. These values have been observed for [AsF₆][−] anions in literature.^{28,31,32}

Theoretical Study

For **FHA** (**1**), **FHA-F** (**2**), and the free [FHA-1H]⁺ cation, quantum chemical calculations were performed. The gas-phase

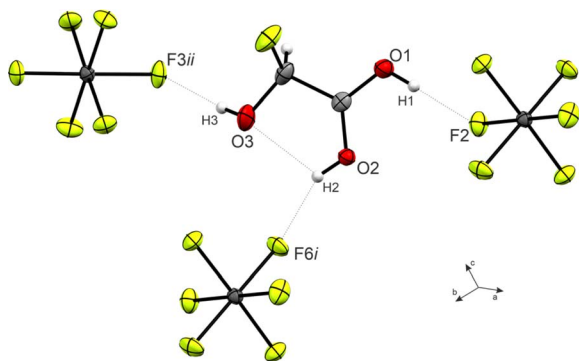


Fig. 3 Hydrogen bonds in the crystal packing of **3** (50% probability displacement ellipsoids, hydrogen atoms displayed as spheres of arbitrary radius).

Table 4 Calculated bond distances (Å) of **FHA**, **FHA-F**, and [FHA-1H]⁺ compared to the experimental values of **3** obtained from the X-ray structure analysis

	FHA ^a	FHA-F ^a	[FHA-1H] ⁺ ^a	X-ray (3)
C1–O1	1.201	1.180	1.268	1.258(4)
C1–O2/F2	1.338	1.342	1.268	1.272(4)
C1–C2	1.532	1.529	1.538	1.515(5)
C2–O3	1.376	1.373	1.368	1.355(5)
C2–F1	1.392	1.389	1.367	1.376(5)

^a Calculated on the B3LYP/aug-cc-pVTZ level of theory.

structures were optimized and the vibrational frequencies were computed on the B3LYP/aug-cc-pVTZ level of theory. In the case of the cation, a direct comparison to the experimental X-ray values is possible. The bond lengths are listed in Table 4. The calculated structures are illustrated together with the cation of **3** in Fig. 4. The labeling of the atoms is based on the crystal structure analysis for consistency.

The C–O bond distances of the protonated carboxy group are in fair agreement with the experimental values. For **FHA**, the values are consistent with comparable carboxylic acids like **GAM** or difluoroacetic acid.^{26,33} The C=O bond length of **FHA-F** is the shortest among the investigated, yet it is in agreement with structural analyses of gaseous acyl fluorides reported in the literature, as well as the C(O)F bond.^{34,35} The C2–O3 distances of all calculated structures (1.368–1.376 Å) are similar, while the X-ray data of **3** is a little shorter. However, all these values are shorter than a regular C–O single bond in primary alcohols (1.426 Å).²⁷ The calculated C2–F1 bond lengths of **FHA** and **FHA-F** are longer than in the case of [FHA-1H]⁺. The bond distances of α -fluoroalcohols compared to regular C–F and C–OH bonds have been discussed in a study by Krossing *et al.* Accordingly, the elongation of the C–F bond is suspected to be a result of lone-pair conjugation of the oxygen atom into the antibonding $\sigma^*(\text{C–F})$ orbital, subsequently shortening the C–OH bond.⁷ This is in agreement with our DFT results. We performed NBO

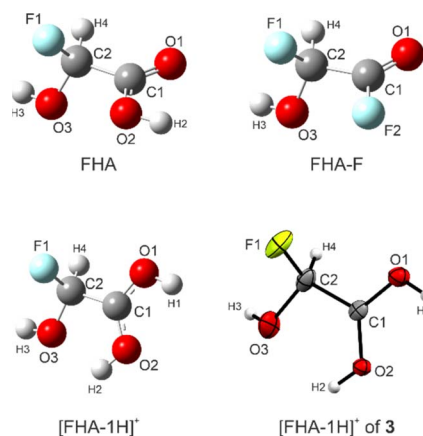


Fig. 4 Optimized gas-phase structures of **FHA**, **FHA-F**, [FHA-1H]⁺, and the cation [FHA-1H]⁺ of **3**. Calculated on the B3LYP/aug-cc-pVTZ level of theory.



Table 5 The stabilization energy by the non-bonding lone-pairs (n) of the O3 and the F1 atom. NBO calculations on the MP2/aug-cc-pVTZ level of theory^a

	$n(\text{O3}) \rightarrow \sigma^*(\text{C2-F1})$	$n(\text{F1}) \rightarrow \sigma^*(\text{C1-C2})$
FHA	109.3 kJ mol ⁻¹	16.8 kJ mol ⁻¹
FHA-F	111.5 kJ mol ⁻¹	19.3 kJ mol ⁻¹
[FHA-1H] ⁺	105.7 kJ mol ⁻¹	29.0 kJ mol ⁻¹

^a Calculated on the MP2/aug-cc-pVTZ level of theory.

calculations of all three investigated compounds (MP2/aug-cc-pVTZ level of theory) to assess this effect. The stabilization energies according to the second-order perturbation theory analyses of these interactions are summarized in Table 5.

The interactions of the oxygen lone-pair with the $\sigma^*(\text{C-F})$ orbital are similar among the investigated compounds, explaining the shortening of the C–OH bond. The C–F distance of the neutral compounds FHA and FHA-F is subsequently elongated. In the case of the protonated species, the calculated C–F bond length rather coincides with a regular distance. Since the protonation has no significant influence on the described interaction, there must be another that strengthens the C–F bond. This is found to be the donation of a fluorine lone-pair into the $\sigma^*(\text{C-C})$ orbital. The stabilization energy of this interaction in [FHA-1H]⁺ is calculated to be 12.2 kJ mol⁻¹ higher than in FHA. This also explains why the C–C bond of the protonated species is the longest. However, the calculation estimates it longer than the experimental X-ray data shows. Similarly, the C–C bonds of FHA (1.532 Å) and FHA-F (1.529 Å) are longer than expected when compared to the corresponding bonds in difluoroacetic acid and difluoroacetyl fluoride.³⁵ This indicates that solid-state effects might have an additional influence on the bond distances.

Conclusions

For the first time, α -fluorohydroxyacetic acid (FHA), its acyl fluoride (FHA-F), and its protonated species ([FHA-1H]⁺) are described. The syntheses of FHA and FHA-F are achieved by reacting glyoxylic acid monohydrate (GAM) with HF/SF₄. By applying the binary superacid HF/AsF₅, [FHA-1H][AsF₆] is the only organic compound, allowing a complete characterization by NMR, vibrational spectroscopy, and single-crystal X-ray diffraction. The superacidic deoxyfluorination only occurs when three equivalents of Lewis acid are used, implying that the superelectrophile [C₂(OH)₃H]²⁺ is formed intermediately. NBO calculations reveal a complex relation between the C–F and the C–OH bond of the fluorohydroxy group. The use of superacids in aHF could enable convenient access to fluorinated compounds with a high electrophilicity and give deoxyfluorination reagents a new appeal.

Data availability

The data supporting this article have been included as part of the ESI.† For full details on vibrational spectroscopy, NMR

spectroscopy, X-ray diffraction refinement, and computational details see the ESI.† Crystallographic data for [CH(OH)FC(OH)₂][AsF₆] has been deposited at the CCDC under the accession number 2173682 and can be obtained from <http://www.ccdc.cam.ac.uk>.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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