Keywords: heterocycles · nitrogen · sulfur · titanium

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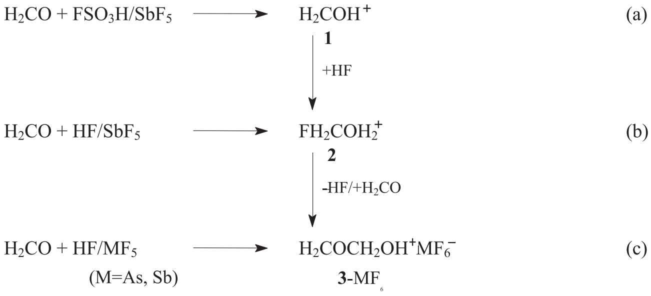
Formaldehyde in Super Acids: A Succession of Products from Carbenium through Oxonium Ion to Hydroxymethyl(methylidene)oxonium Salts

Rolf Minkwitz,* Stefan Schneider, and Hans Preut

The products of the reaction of formaldehyde with super acids were first examined by G. A. Olah et al.[1] The hydroxycarbonium ion **1** was identified in FSO_3H/SbF_5 [Eq. (a)] by NMR spectroscopy, and fluormethyloxonium ions **2** [Eq. (b)] were found after addition of HF or directly in HF/SbF_5.[2, 3] We attempted to isolate salts of monofluoromethanol, which is unknown in pure substance, from the HF solution according to Equation (b). Surprisingly, we obtained hydroxymethyl(methylidene)oxonium hexafluorometalate **3**-MF_6 at −78°C according to Equation (c) but no polymerization product of formaldehyde, as proposed by G. A. Olah et al.[3]



$$H_2CO + FSO_3H/SbF_5 \longrightarrow \underset{\mathbf{1}}{H_2COH^+} \qquad (a)$$

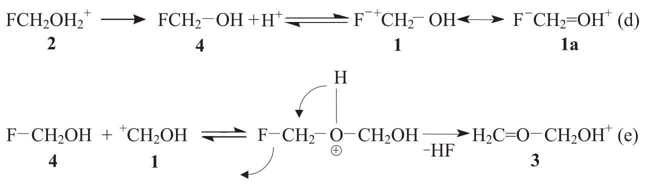
$$\downarrow +HF$$

$$H_2CO + HF/SbF_5 \longrightarrow \underset{\mathbf{2}}{FH_2COH_2^+} \qquad (b)$$

$$\downarrow -HF/+H_2CO$$

$$\underset{(M=As,\ Sb)}{H_2CO + HF/MF_5} \longrightarrow \underset{\mathbf{3}\text{-}MF_6}{H_2COCH_2OH^+MF_6^-} \qquad (c)$$

The formation of cation **3** might proceed in a simple way upon addition of formaldehyde to protonated formaldehyde **1**. However, no indications for **1** were found in the NMR spectra of the HF solution. Only signals for **2**, which exclusively exists in solution, were observed ($\delta(^{13}C) = 100.4$, $^1J_{C,F} = 222$ Hz); this confirms previous results by Olah et al. The stabilization in solution of protonated molecules for which the unprotonated form cannot be found is known and was recently described by Olah et al. for the example of protonated fluoroformic acid.[3, 4] The existence of cation **3** in solution cannot be proved. Considering the NMR spectroscopic results, it seems more likely that **3** is formed from **2** by a reversible electrophilic addition with subsequent elimination of HF [Eqs. (d) and (e)]. With the exception of **2**, no experimental proof was found for the intermediates which are formally required.



$$\underset{\mathbf{2}}{FCH_2OH_2^+} \longrightarrow \underset{\mathbf{4}}{FCH_2{-}OH} + H^+ \rightleftharpoons \underset{\mathbf{1}}{F^{-}\,{}^{+}CH_2{-}OH} \longleftrightarrow \underset{\mathbf{1a}}{F^{-}CH_2{=}OH^+} \qquad (d)$$

$$\underset{\mathbf{4}}{F{-}CH_2OH} + \underset{\mathbf{1}}{{}^{+}CH_2OH} \rightleftharpoons F{-}CH_2{-}\overset{H}{\underset{\oplus}{O}}{-}CH_2OH \xrightarrow[-HF]{} \underset{\mathbf{3}}{H_2C{=}O{-}CH_2OH^+} \qquad (e)$$

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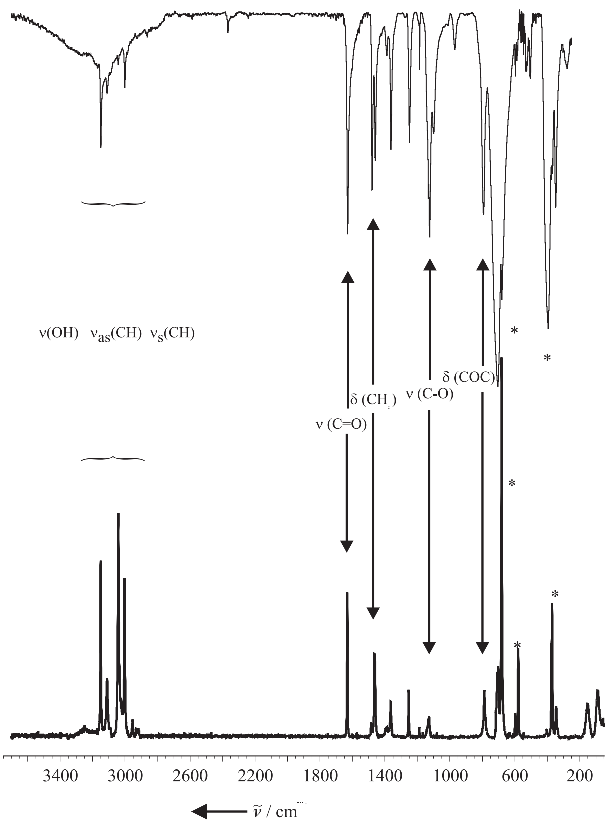

Figure 1. IR (top) and Raman spectra (bottom) of **3**-AsF_6 with labels for some vibrations of the cation. Vibrations of the anion are labeled with an asterisk. The IR spectrum was measured with a neat sample on a CsI plate at 233 K, and the Raman spectrum at 195 K.

Compounds **3**-MF_6 precipitate as colorless salts at either −40 °C on concentrating the solution by removing HF or on cooling the solution to −78 °C. Vibrational spectroscopy provided the first indications for the presence of **3**, which was confirmed by a crystal structure analysis. The vibrational frequencies of **3** are in the expected range for molecules with comparable groups of atoms.[5] The symmetric and antisymmetric valence vibrations of the two CH_2 groups of the cation can be clearly distinguished in the Raman and IR spectra (Figure 1, Table 1).: ν_{as} for the methylidenic protons is observed at 3150 cm^{-1} (IR) and ν_s at 3041 cm^{-1} (Raman); ν_{as} for the methylic protons is at 3111 cm^{-1} (IR) and ν_s at 3002 cm^{-1} (Raman). Even if all work with DF/MF_5 systems is performed quickly, H/D exchange cannot be avoided.

In the crystalline state, cations and anions of **3**-MF_6 are connected by short $H\cdots F$ distances—the shortest interionic $H\cdots F$ contact is 217(8) pm (sum of the van der Waals radii 267 pm)—and a three-dimensional network is formed (Figure 2, Table 2).[6] In the C−O=C skeleton of **3** the lengths of the C(1)−O(1) single bonds and the C(2)−O(1) double bonds are increased compared to those in dimethyl ether (C−O 141.0 pm) or formaldehyde (C=O 120.8 pm).[7, 8]

The simplest molecule with a C−O=C skeleton is the methoxymethyl ion, $H_3COCH_2^+$, for which several ab initio calculations are known.[9–11] Values of 147.8 to 149.3 pm for the C−O bond and 121.5 to 124.0 for the C=O bond were calculated; corresponding bond angles values of 121.3 to 124.5° were predicted.[11] The C(2)-O(1)-C(1) bond angle and the C−O bond lengths in cation **3** are comparable with values predicted by ab initio methods.

Table 1. Vibrational frequencies [cm^{-1}] of $(X_2C^1OC^2X_2OX)MF_6$ [**3**-MF_6; M = As,Sb, X = H,D] and tentative assignments.[a]

M = As, X = H		M = Sb, X = H		M = As, X = H,D		M = Sb, X = H,D		Tentative assignment
Raman	IR	Raman	IR	Raman	IR	Raman	IR	
3250 vw	3250 b							ν(OH)
3149 m	3150 w	3150 vw	3120 sb	3151 m	3158 vw	n. d.[b]	n. d.[b]	$\nu_{as}(C^1H)$
3110 w	3111 vw	3112 vw		3113 m	3120 vw	n. d.[b]	n. d.[b]	$\nu_{as}(C^2H)$
3041 m	3033 vw	3041 w		3043 s	3051 vw	3030 m	3036 w	$\nu_s(C^1H)$
3002 m	3002 vw	3002 w		3003 m	3013 vw	2985 m	2990 w	$\nu_s(C^2H)$
				2404 w	2409 m	2404 w	2409 m	ν(OD)
				2345 w		2331 m	2333 m	ν_{as}(CD)
				2307 m	2317 vw	2288 m	2294 m	ν_s(CD)
1632 m	1629 m	1629 vw	1626 m	1629 m	1634 m	n. d.[b]	1637 m	ν(C=O)
			1480 m	1483 w	1484 w	1483 w	1484 m	$\delta(CH_2)$
1464 w	1459 w	1461 vw	1455 m	1461 m	1468 w			$\delta(CH_2)$
1393 vw								$\delta(CH_2)$
1364 vw	1362 w	1364 vw	1364 w	1365 w	1369 m	1330 w		δ(COH)
1254 w	1249 w	1263 vw	1239 w	1258 w	1254 m	1271 w		δ(HCO)
		1185 vw	1193 vw	1194 vw	1201 m	1196 w	1201 m	$\tau(CH_2)$
1130 vw	1132 w	1131 vw	1132 m	1135 w	1132 m			ν(C−O)
			1102 w	1097 w	1101 w	1092 w		ν_{as}(C−O)
		803 w	803 w	792 m	803 m			$\rho(CH_2)$, δ(COC)
		564 w	563 w	567 m	558 m	561 m	558 m	$\rho(CH_2)$
				353 m	360 m	281 w		$\omega(CH_2)$
				166 m				
682 vs		653 vs		685 vs		647 vs		$\nu(MF_6^-)$
580 w		577 w		580 m		592 m		$\nu(MF_6^-)$
	704 vs		666 vs		709 vs		666 vs	$\nu(MF_6^-)$
	394 s		282 s		398 s		291 s	$\delta(MF_6^-)$
371 m		289 m		380 m		384 m		$\delta(MF_6^-)$

[a] Definitions of abbreviations: vw: very weak, w: weak, m: medium, s: strong, vs: very strong, b: broad. [b] Not determined.

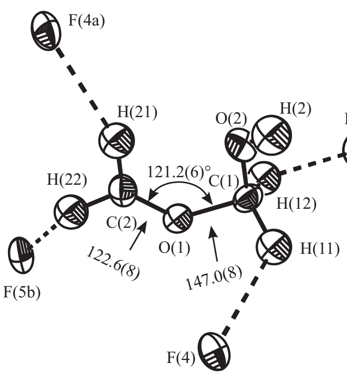

Figure 2. Structure of the cation **3** in the crystal with contacts, atom labels, and structural parameters for the central unit. Further distances [pm]: F4a ⋯ H21 236(8), F5b ⋯ H22 217(8), F6c ⋯ H12 244(8), F4 ⋯ H11 240(9). Symmetry operations: $x-1, +y, +z$ (a), $-x+1, -y, -z+1$ (b), $x, -y-0.5, +z+0.5$ (c).

Table 2. Selected bond lengths [pm] and angles [°] for **3**-AsF_6. Not all the atoms of the anion are shown in Figure 2.[a]

As(1)–F(2)	171.8(4)	C(2)-O(1)-C(1)	121.2(6)
As(1)–F(4)	171.0(4)	O(2)-C(1)-O(1)	108.8(5)
As(1)–F(6)	170.2(5)	F(1)-As(1)-F(4)	89.6(2)
O(1)–C(2)	122.6(8)	F(6)-As(1)-F(4)	90.4(3)
O(1)–C(1)	147.0(8)	F(1)-As(1)-F(2)	179.2(2)
O(2)–C(1)	132.5(8)		

[a] The standard deviations refer to the last digit.

Experimental Section

H_2CO was obtained and purified according to ref. [12]. AsF_5 was obtained by allowing the elements to reaction and purified by fractional condensation. SbF_5 was purified by fractional distillation, and HF was dried with fluorine.[13]

In a KEL-F reactor MF_5 (3 mmol; M = As, Sb) was dissolved in HF (≈ 5 g). The solution was frozen at −196 °C, and then H_2CO (3 mmol) condensed onto the solution. The reaction mixture was allowed to warm slowly to −40 °C. The excess reactant was removed either at −78 °C or at −40 °C under a dynamic vacuum. Compound **3**-MF_6 remained as a colorless solid.

Instruments: Raman: Jobin–Yvon T64000, Ar^+ laser ($\lambda = 514.5$ nm) Spectra Physics; IR: Bruker IFS 133v; NMR: Bruker DPX300.

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Matrix Isolation and Characterization of a Reactive Intermediate in Olefin Oxidation with Chromyl Chloride**

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Although the oxidation of organic substrates by Cr^{VI} compounds has always been a useful tool in the hands of chemists, the course of such reactions and the nature of the intermediates have remained for the most part unknown. For example, the mechanism of C–H activation in the Etard reaction,[1] known since 1877, was only revealed in detail in 1995.[2] In the past, complex mechanisms were put forward for the oxidation of olefins with chromyl chloride CrO_2Cl_2[3, 4] that attempted to explain the great variety of products obtained on the basis of widely differing intermediates such as chromaoxetanes, chromium alkoxides, and epoxide complexes. None of these intermediates has ever been proven. The occurrence of carbonyl compounds among the products was explained by rearrangements of certain products during work-up,[3, 5] whereas more recent work highlights the relevance of intermediate chromium complexes of these carbonyl compounds. For example, ethylene reacts with the CrO_2^+ ion in the

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