Articles

Halogenated Carboxonium Salts: Preparation and Structural Analysis

Rolf Minkwitz,*,† Stefan Reinemann,† Oliver Blecher,† Hans Hartl,*,‡ and Irene Brüdgam‡

Anorganische Chemie, Fachbereich Chemie der Universität Dortmund, D-44221 Dortmund, Germany,
and Institut für Anorganische und Analytische Chemie der Freien Universität Berlin,
D-14195 Berlin, Germany

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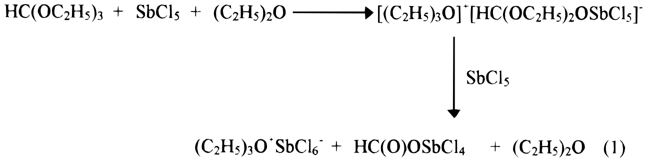
We have studied the preparation and isolation of the halogenated alkylidene oxonium salts $CH_3OCHX^+MF_6^-$ (X = Cl, F; M = As, Sb). Addition of dichloromethylmethylether at −78 °C to the superacidic media HF/MF_5 resulted in the formation of the chlorine compounds $CH_3OCHCl^+MF_6^-$, whereas at −65 °C the fluorinated salts $CH_3OCHF^+MF_6^-$ are formed by a chlorine/fluorine exchange. The salts are characterized by their low-temperature IR and Raman spectra. Additionally, the crystal structures of the hexafluoroantimonates are presented. The structures of the cations turned out to be different in some points. The salt $CH_3OCHF^+SbF_6^-$ crystallizes in the monoclinic space group $P2_1/c$ with 4 molecules in the unit cell and $a = 9.942(2)$, $b = 7.454(2)$, and $c = 10.297(3)$ Å; $\beta = 111.27(2)°$. The salt $CH_3OCHCl^+SbF_6^-$ crystallizes in the monoclinic space group $P2_1/c$ with 4 formula in the unit cell and $a = 5.970(3)$, $b = 12.019(5)$, and $c = 10.994(5)$ Å; $\beta = 92.59(3)°$.

Introduction

Tertiary oxonium salts are well-known and have already been extensively examined by Meerwein et al.[1−5] The saturated trialkyl oxonium salt $(C_2H_5)_3O^+SbCl_6^-$, for example, was prepared by the reaction of $SbCl_5$ with a mixture of $HC(OC_2H_5)_3$ and diethyl ether (eq 1).[3]



"Unsaturated" tertiary oxonium salts of the general form $R_2COR^+BF_4^-$ (R,R = alkyl, aryl), which were also isolated by Meerwein (eq 2),[3] are excellent examples for the discussion of a carbenium−oxonium mesomerism.

$$3\,R_2C(OR')_2 + 4BF_3 \rightarrow 3[R_2\overset{+}{C}{-}OR' \leftrightarrow R_2C{=}\overset{+}{O}R']BF_4^- + B(OR')_3 \quad (2)$$
$$(R,R' = \text{alkyl, aryl})$$

An alternative way to obtain such "unsaturated" oxonium salts, also named as alkylidene oxonium salts, is described by Klages et al. by halogen abstraction from methyl(α-chloroalkyl) ethers (eq 3).[6]

$$RR'C(Cl)OCH_3 + SbCl_5 \rightarrow RR'COCH_3^+SbCl_6^- \quad (3)$$
$$\text{a: } R = R' = H;\ \text{b: } R = CH_3, R' = H;\ R = R' = CH_3$$

Using the dihalogenated ethers CH_3OCHCl_2 and CH_3OCHF_2 as starting reagents leads to the formation of halogenated alkylidene oxonium salts, which was proved by Olah et al. by NMR experiments (eq 4).[7]

$$CH_3OCHX_2 + SbF_5 \xrightarrow[-60/-40\ °C]{SO_2} CH_3OCHX^+SbF_5Cl^- \quad (4)$$
$$(X = F, Cl)$$

In our working group the superacidic systems HF/MF_5 (M = As, Sb) have proven to be excellent reaction media for the preparation and crystallization of oxonium, peroxonium, and alkylidene oxonium salts.[8−14] The reaction of H_2CO in HF/MF_5, for example, resulted in the unexpected formation of the hydroxymethyl methyliden oxonium salts $H_2C(OH)OCH_2^+MF_6^-$ (eq 5).[13]

$$2H_2CO + HF/MF_5 \xrightarrow[-78\ °C]{HF} \underset{\mathbf{1}}{H_2C(OH)OCH_2^+MF_6^-} \quad (5)$$

In this work we present the isolation of the oxonium salts $CH_3OCHX^+MF_6^-$ (X = Cl, F; M = As, Sb) which are prepared

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‡ Freie Universität Berlin.

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Table 1. Crystal Structure Data for $CH_3OCHCl^+SbF_6^-$ (**2**) and (*Z*)-$CH_3OCHF^+SbF_6^-$ (**3**)

	2	**3**
chemical formula	$C_2H_4ClF_6OSb$	$C_2H_4F_7OSb$
formula weight	319.25	298.80
space group (no.)	$P2_1/c$ (4)	$P2_1/c$ (4)
a (Å)	5.970(3)	9.942(2)
b (Å)	12.019(5)	7.454(2)
c (Å)	10.994(5)	10.297(3)
β (deg)	92.59(3)	111.27(2)
V (Å^3)	788.1(6)	711.1(3)
T (K)	125	125
λ (Å)	0.71069	0.71069
δ_{calcd} (g cm^{-3})	2.657	2.791
μ (cm^{-1})	38.91	39.59
R^a	0.042	0.047
$R_w{}^a$	0.134	0.144

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. Refinement method: full-matrix least-squares calculations based on F^2.

Table 2. Selected Bond Lengths (pm) and Angles (deg) for $CH_3OCHX^+SbF_6^-$ (X = F (**3**), Cl (**2**))

2		**3**	
O−C(2)	125.2(9)	O−C(2)	122.4(9)
O−C(1)	151.7(9)	O−C(1)	147.9(9)
C(2)−Cl	165.0(9)	C(2)−F(7)	126.9(7)
C(2)−O−C(1)	115.7(6)	C(2)−O−C(1)	120.7(5)
O−C(2)−Cl	117.3(6)	O−C(2)−F(7)	121.9(7)
		O−C(2)−H(2)	116.4(75)
		F(7)−C(2)−H(2)	121.6(76)

by adding $H_3COCHCl_2$ to the superacidic media HF/MF_5. The effects of different halogenation at the methylidene fragment on bonding properties are demonstrated by the crystal structures of the hexafluoroantimonates. The $CH_3OCHX^+MF_6^-$ salts are further characterized by their low-temperature IR and Raman spectra.

Experimental Section

All reactions were carried out using KEL-F reactors and a stainless steel vacuum apparatus. HF was dried with fluorine. Nonvolatile compounds were handled in a dry N_2 atmosphere by using standard Schlenk techniques.

IR spectra were recorded on a Bruker IFS 113v spectrometer in a low-temperature cell between CsI plates.[15] Raman spectra were run on a Jobin-Yvon T64000 (Instruments SA) equipped with an Ar^+ laser (Spectra Physics) operating at 514.5 nm.

The NMR spectra in HF solution at −65 °C were recorded with a Bruker DPX 300 spectrometer relative to TMS and F11 as external standards.

Preparation of $CH_3OCHX^+MF_6^-$ (X = Cl, F; M = As, Sb). $CH_3OCHCl^+MF_6^-$ (2). A 3-mL aliquot of HF was condensed in a KEL-F reactor with 1 mmol of MF_5 (M = As, Sb). After 1 h at −78 °C, an equimolar amount of CH_3OCHCl_2 was added at −196 °C. Vacuum removal of the HF at −78 °C resulted in colorless and crystalline solids.

$CH_3OCHF^+MF_6^-$ (3) was isolated by nearly the same procedure with the exception that the reaction mixture was warmed to -65 °C.

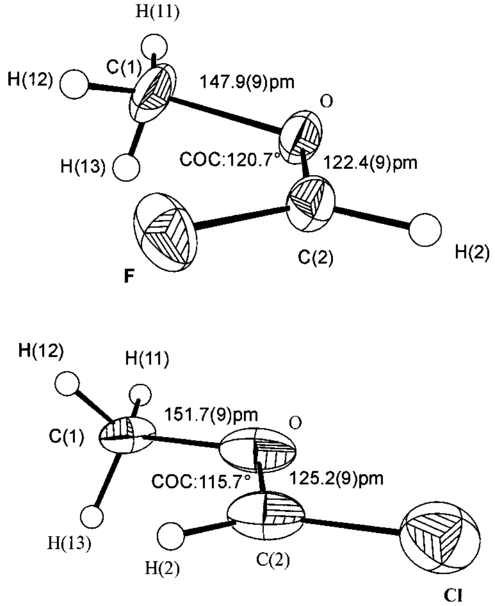

Figure 1. Structures of the cations CH_3OCHX^+ (X = Cl, F) with atom labels and structural parameters for the central unit. Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Comparison of the CO Bond Lengths (pm) and the COC Angles (deg) for the Salts $CH_3OCHX^+SbF_6^-$ (X = F (**3**), Cl (**2**)) and $H_2C(OH)OCH_2^+AsF_6^-$ (**1**)[11]

	C=O	C−O	C−O−C
$H_2C(OH)OCH_2^+AsF_6^-$	122.6(8)	147.0(8)	121.2(6)
$CH_3OCHF^+SbF_6^-$	122.4(9)	147.9(9)	120.7(5)
$CH_3OCHCl^+SbF_6^-$	125.2(9)	151.7(9)	115.7(6)

X-ray Crystallography. Crystals of **2** and **3** were mounted on glass fibers with paraffin oil. Crystallographic information for both compounds is listed in Table 2. Intensity data (Mo Kα radiation, $\omega-2\theta$ scans, 125 K) were converted to structure-factor amplitudes and their esds by correction for background, scan speed, crystal decay, Lorentz, and polarization effects. Experimental absorption correction was applied to the data of **3** (psi scans) and empirical adsorption correction (DIFABS) to that of **2**. The structures were solved by direct methods and refined via standard least-squares and Fourier techniques. The positions of all non hydrogen atoms were refined with anisotropic thermal parameters. All H-atom positions of **3** and the H(2) atom of **2** were placed by difference Fourier technique; the missing H atoms were placed at calculated sites. Further details of the X-ray structural determinations are located in the Supporting Information.

Formation and Stability. Dichloromethylmethylether reacts at −78 °C in the superacid system HF/MF_5 (M = As, Sb) under formation of $CH_3OCHCl^+MF_6^-$ and HCl (eq 6). Hydrogen chloride can be detected by IR spectroscopy. The salts are barely soluble in SO_2 and HF (−78 °C) and insoluble in SO_2ClF and CH_2Cl_2.

$$H_3COCHCl_2 + HF/MF_5 \xrightarrow[-78\ °C]{HF} \underset{\mathbf{2}}{H_3COCHCl^+MF_6^-} + HCl \quad (6)$$

Warming the reaction mixture from −78 to −65 °C resulted in the formation of the fluorocation CH_3OCHF^+ which can be observed by ^{19}F and ^1H NMR spectroscopy. The chemical shifts and the coupling constants are identical with those already observed by Olah.[7] Removal of the solvent yields the $CH_3OCHF^+MF_6^-$ salts in quantitative amounts. These salts are soluble in HF, barely soluble in SO_2, and insoluble in SO_2ClF and CH_2Cl_2.

$$H_3COCHCl_2 + HF/MF_5 \xrightarrow[-65\ °C]{HF} \underset{\mathbf{3}}{H_3COCHF^+MF_6^-} + 2HCl \quad (7)$$

The colorless and crystalline solids are stable up to −45 °C ($CH_3OCHCl^+SbF_6^-$), −50 °C ($CH_3OCHCl^+AsF_6^-$), −30 °C (CH_3OCHF^+-

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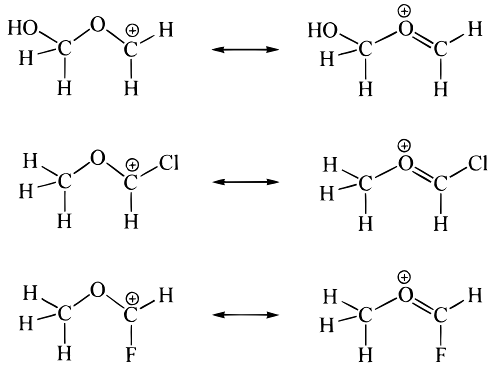
Table 4. Vibrational Frequencies (cm^{-1}) for $CH_3OCHX^+MF_6^-$ (X = Cl, F; M = As, Sb)

$CH_3OCHF^+AsF_6^-$		$CH_3OCHF^+SbF_6^-$		$CH_3OCHCl^+AsF_6^-$		$CH_3OCHCl^+SbF_6^-$		
IR	RA	IR	RA	IR	RA	IR	RA	assignmt
3070 w	3074 (18)	3076 w	3067 (17)	3065 w	3065 (19)	3071 m	3065 (13)	
	3043 (15)		3045 (15)				3048 (10)	$\nu(CH_3)$
	2994 (38)		2998 (29)		2994 (22)		2990 (25)	
1578 s	1574 (4)	1571 m	1581 (5)	1579 m	1573 (6)	1579 m	1583 (8)	$\nu(C{=}O)$
1449 w		1450 m						
1387 m	1393 (5)	1390 m	1396 (4)	1385 m	1394 (5)	1384 w	1390 (3)	$\delta(CH_3)$
1340 m	1351 (7)	1344 m	1352 (5)	1350 m	1356 (4)	1340 w	1352 (4)	
1257 m		1260 m						$\nu(CF)$
953 m	952 (3)	949 m	952 (2)					
919 w	925 (3)	925 m	927 (2)	928 m	924 (2)	922 w	925 (2)	$\nu(C{-}O)$
780 m	787 (1)	789 sh	780 (2)		767 (2)	775 m	769 (3)	$\delta(HCO)$
					684 (15)		687 (11)	$\nu(C{-}Cl)$
441 m	449 (11)	445 m	450 (9)	443 w	447 (8)	441 w	445 (3)	$\delta(HCO)$
	386 sh	382 w	392 sh		383 sh	379 w	382 sh	$\delta(COC)$
					290 (3)		296 (3)	$\delta(HCCl)$
218 w	222 (1)	221 w	221 (2)		235 (2)		235 (1)	
	193 (1)		197 (2)		195 (2)		195 (1)	def
	111 (2)		116 (1)					
695 vs		674 vs		692 vs		672 vs		
	690 (100)		652 (100)		687 (100)		654 (100)	
	585 (14)		587 (13)		583 (15)		581 (20)	$\nu(MF_6^-)$
394 vs		290 vs		396 vs		292 vs		
	376 (33)		292 (34)		377 (34)		286 (32)	

Scheme 1



SbF_6^-), and −35 °C ($CH_3OCHF^+AsF_6^-$). When thermolyzed, HCl/HF, CH_3F, and MF_5 can be identified as decomposition products by IR spectra in gaseous phase.

Crystal structures of (*E*)-$CH_3OCHCl^+SbF_6^-$ (2) and (*Z*)-$CH_3OCHF^+SbF_6^-$ (3). Even though compound 2 as well as compound 3 crystallizes in the monoclinic space group $P2_1/c$, the compounds are not isostuctural (Tables 1 and 2). The halogen atoms and the methyl group are trans-configured in the chlorocation and cis-configured in the fluorocation (Figure 1). Both cations show a nearly planar arrangement of the atoms C(1), O, C(2), H(2), and F or Cl (maximum displacements from the least-squares planes are 6(3) pm in **2** and 1(2) pm in **3**; the torsion angles F(1)/Cl−C(2)−O−C(1) are 179.0(5)° in **2** and 2.84(6)° in **3**.

In discussing a carbenium−oxonium mesomerism (Scheme 1) the main interest concerns the CO bond lengths. In Table 3 the CO bond lengths and COC angles of **2** and **3** are compared with those previous determined for $H_2C(OH)OCH_2^+AsF_6^-$ (**1**).[13] The C═O bond distance of **2** (125.2(9) pm) is slightly longer than that of **3** (122.4(9) pm), which is comparable to that of **1** (122.6(8) pm). The COC (120.7(5)°) angle in **3** corresponds, within the 3σ range, with an ideal 120° angle, as expected for sp^2 hybridization of the oxygen atom. In this aspect, **3** is nearly identical with **1** (COC: 121.2(6)°), whereas in **2** a COC angle of 115.7(6)° is found. Compared to the formyl compounds O═CHCl (C−Cl: 176.8 pm)[16] and O═CHF (C−F: 131.4 pm)[17] in **2** (165.0(9) pm) as well as in **3** (126.9(7) pm), shorter halogen−carbon bond distances are observed. Relative to OCHCl and OCHF, observed C−X bond shortening is 6.7% for **2** and 3.4% for **3**.

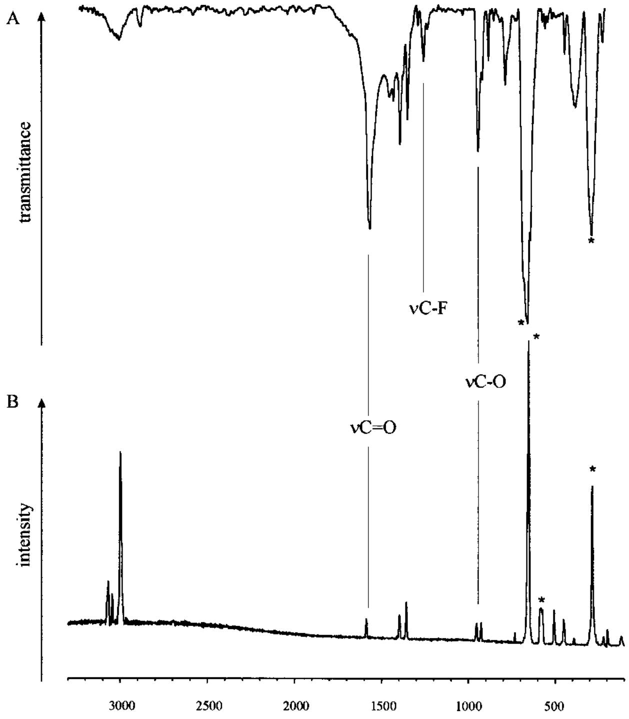


Figure 2. Low-temperature IR and Raman spectra of $CH_3OCHF^+AsF_6^-$. Anionic vibrations are marked with an asterisk.

Although it is known that the carbenium stabilization by interaction of the empty carbenium p orbital is greater in the case of a fluorine substitution, the above-presented facts indicate that the chlorine compound possesses more carbenium character than the fluorine one.[18]

The positions of the methyl hydrogen atoms of **3** were experimentally determined by difference Fourier syntheses. Though the hydrogen parameters are not of high accuracy, it is certain that there exists a very short intramolecular contact F···H(12) of nearly 240 pm. The structures of both cations are comparable in this respect to those of the molecular compounds CF_3NCHCl and CF_3NCHF, existing as *E* and *Z*

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isomers.[19] Intramolecular contacts F- -H are the reason that the *E* isomers are predominant. Similar attractive contacts could be responsible for the cis configuration of **3**.

In **2** as well as in **3**, relatively long intermolecular contact distances O···F > 290 pm are found. The SbF_6^- anions in both compounds show only small deviations from regular octahedral symmetry.

Vibrational Spectra. With the exception of the ν(C−X) stretching mode, the IR and Raman spectra of the chlorine and fluorine species are very similar. Representative for the $CH_3OCHX^+MF_6^-$ salts (X = Cl, F; M = As, Sb), the low-temperature IR and Raman spectra of $CH_3OCHF^+AsF_6^-$ are shown in Figure 2. The observed IR and Raman frequencies of $CH_3OCHX^+MF_6^-$ are summarized in Table 4 along with their assignments.

The ν(C−H) stretching modes are registrated in the region of 3076−2990 cm^{-1}. In comparison to $H_3COCHCl_2$ the ν(C−H) modes shift to higher frequencies.[20] This is in good agreement with the ν(CH) stretching modes of the previously investigated $H_2C(OH)OCH_2^+$ (**1**) cation at 3149−3002 cm^{-1}.[13]

The IR spectra of **2** and **3** show intense bands at 1571 and 1579 cm^{-1} which are assigned to the ν(C=O) stretching modes. In comparison with **1** (ν(C=O): 1680 cm^{-1}) the unusual low ν(C=O) frequencies in **2** and **3** are caused by the direct influence of the halogen atoms on the methyliden fragment.

The C−F stretching mode of **3** at 1260 cm^{-1} is located in the expected region.[19−21] It is comparable to the vibrational results obtained for the molecular nitrogen compound, CF_3NCHF. The ν(C−Cl) frequency of **2** is assigned to the intensive Raman line at 687 cm^{-1}, whereas it is not possible to fix it in the IR spectra because of a spectral overlap by the anion.

The anionic ν(M−F) stretching modes do not show any spectroscopic splitting as the anions possess nearly regular octahedral geometry in both $CH_3OCHX^+SbF_6^-$ salts.

Conclusion

The halogenated carboxonium salts have been isolated for the first time. The comparison of the cationic structures in **2** and **3** gives important information for the understanding of the carbenium oxonium mesomerism. The CO bond lengths and the COC angles reveal slightly more carbenium character for the chlorine compound.

Supporting Information Available: Listings of crystal data and intensity collection parameters, anisotropic thermal parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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