Trihydroxycarbenium Hexafluorometalates: Salts of Protonated Carbonic Acid

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Dedicated to Professor Wolfgang Sawdony
on the occasion of his 65th birthday

The work of G. A. Olah on the feasibility of protonation of extremely weak bases has stimulated interest in this area of research, as highlighted recently by T. S. Sorensen.[1]

The trihydroxycarbenium ion, $C(OH)_3^+$ (**1**), which is isoelectronic with orthoboric acid, was up to now only confirmed by NMR spectroscopy as a compound of the reaction mixture of the protonation of carbonates or hydrogen carbonates with the superacid FSO_3H/SbF_5.[2] Since carbonic acid is not available as a reactant,[3, 4] we used, as for the synthesis of protonated hydrogen peroxide,[5] carbonic acid bis(trimethylsilyl) ester for the reaction with the superacids HF/MF_5 (M = As, Sb) according to Equation (1).

$$OC(OSiMe_3)_2 + HF/MF_5 \rightarrow \underset{\mathbf{1}\text{-}MF_6}{C(OH)_3^+MF_6^-} + Me_3SiF \qquad (1)$$

The NMR spectra (in HF at −60 °C: $\delta(^1H) = 11.7$, $\delta(^{13}C) = 166.8$)[2, 7] confirm that the trimethylsilyl groups are removed leading to the formation of compound **1**. Whereas the HSO_3F/SbF_5 system contains no readily volatile components, in this case the excess HF, which also serves as solvent, as well as the Me_3SiF which is formed in the reaction can be removed at −78 °C under vacuum. The moisture-sensitive salts decompose quantitatively into CO_2 and $H_3O^+MF_6^-$ above −16 °C in the case of **1**-AsF_6 and above −4 °C in the case of **1**-SbF_6. The decomposition proceeds by removal of water from **1**. This requires a 1,3 proton shift, for which a remarkable energy barrier of 238 kJ mol^{-1} was calculated.[8] The surprising stability of the trihydroxycarbenium ions was already explained by resonance stabilization via onium ions.[2]

The vibrational spectra of the salts of **1** are congruent with the spectra of the isoelectronic boric acid (Table 1, Figure 1).[9] In the Raman spectra, unlike in the IR spectra, the vibrations of the cations can only be observed at very low intensities. By assuming C_{3h} symmetry for **1** all vibrational frequencies can be assigned in analogy to those of the boric acid; however, owing to the positive charge of **1** the vibrational frequencies are shifted on average by 200 cm^{-1} to higher wavenumbers, in comparison to those of boric acid. The symmetric C–O

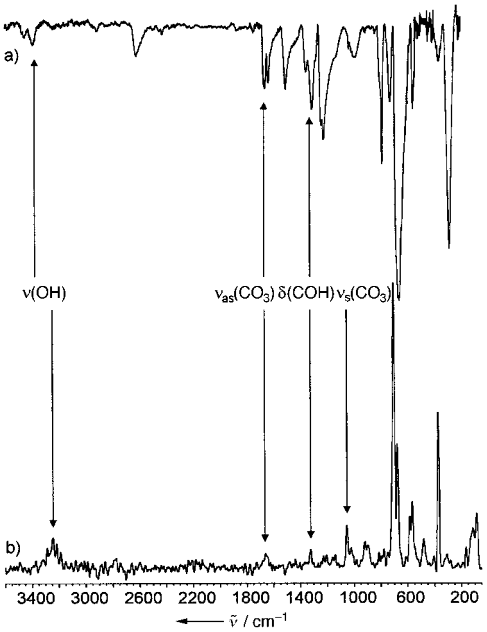

Figure 1. a) IR spectrum of **1**-SbF_6 (−40 °C) and b) Raman spectrum of **1**-AsF_6 (−70 °C) of the solid compounds.

Table 1. Vibrational frequencies [cm^{-1}] of $C(OX)_3^+$ (X = H, D) and assignment.[a]

$B(OX)_3$[11]		$C(OH)_3^+$				$C(OD)_3^+$				Assignment
		SbF_6^-		AsF_6^-		SbF_6^-		AsF_6^-		(X = H, D)
X = H	X = D	Raman	IR	Raman	IR	Raman	IR	Raman	IR	
3245	2434		3457 vw		3409 b		2496 m		2486 w	$\nu_{as}(OX)$
3220	2400		3390 vw							$\nu_{as}(OX)$
3168	2377	n.o.		3254 wb		2382 m		2386 mb		$\nu_s(OX)$
1440	1415		1663 w	1661 vw	1661 w	1630 vw	1633 w		1635 w	$\nu_{as}(CO_3)$
1365	1225		1635 w		1629 w		1611 w	1620 vw	1615 w	$\nu_{as}(CO_3)$
1185	910		1352 w	1330 vw	1349 w		1199 w		1197 w	$\delta(COX)$
1163	1013	1310 vw	1307 w		1309 w		1182 w	1258 vw	1185 w	
1077	835	1232 vw	1238 w	1235 vw			1124 w		1138 w	
878	832	1055 m		1056 m		1062 m		1065 m		$\nu_s(CO_3)$
818	650		1037 vw	1028 w	1035 vw		1032 vw		1035 vw	$\tau(COX)$
808	560		989 wb		991 wb	925 vw	987 w	928 w	982 w	$\tau(COX)$
625	665		804 w				801 w			$\gamma(CO_3)$
538	510		786 m	787 vw	785 m		790 m		798 m	$\delta(CO_3)$
498	460	721 m	728 w			722 w	724 w			$\delta(CO_3)$
		650 vs		698 vs		656 vs		698 vs		
			661 vs		704 vs		665 vs		702 vs	$\nu(MF_6^-)$
		570 m		573 m		574 s		567 m		
			283 s		380 s		284 s		389 s	
		285 s		374 s		293 m		374 s		

[a] Vibrations of the anions are not listed; vw: very weak, w: weak, m: medium, s: strong, vs: very strong, b: broad, sh: shoulder, n.o.: not observed.

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stretching vibration, characteristic for ion **1**, is observed in the region between 1055 and 1065 cm^{-1}. According to the vibrational spectra, no reduction in the symmetry of the octahedral hexafluorometalate anions is found; three Raman-active and two IR-active vibrations can be assigned in accordance with O_h symmetry.

The spectroscopic studies of the salts of **1** were complemented by the single-crystal X-ray structure investigation of **1**-AsF_6 (Table 2).[10] The cation **1** shows C_3 symmetry in the solid. The C–O bond lengths of 123.1(4) pm are comparable with those found in the structure of protonated formic acid (125.5(5) and 123.9(6) pm).[11] In contrast in neutral formic acid the C–O double bond is 122.2(2) pm and the C–O single bond is 130.8(2) pm.[12] This leads to the conclusion that the bond order of the C–O bonds in **1** is 1.5, and the positive charge is delocalized over the whole cation. Short interionic contacts (273.7(6) pm) to fluorine atoms of three adjacent anions are made through the oxygen atoms (Figure 2). The hydrogen atoms are also localized along these O$\cdots$F axes. These contacts between cations and anions lead to the formation of a three-dimensional network (Figure 3).

Table 2. Selected bond lengths [pm] and angles [°] of **1**-AsF_6.

As(1)–F(2)	168.2(3)	F(2d)-As(1)-F(2)	91.7(2)
As(1)–F(1)	171.6(3)	F(2)-As(1)-F(1)	89.6(2)
C(1)–O(1)	123.1(4)	F(2c)-As(1)-F(1)	177.6(2)
O(1)–H(1)	88.7	O(1a)-C(1)-O(1)	119.9(1)
O$\cdots$F	273.7(4)	C(1)-O(1)-H(1)	108.6

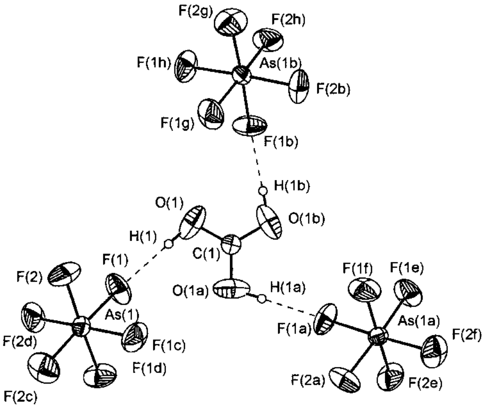

Figure 2. Structure of **1**-AsF_6 in the crystal with interionic contacts and atom labels.

Experimental Section

$(Me_3SiO)_2CO$ was prepared according to reference [6]. AsF_5 was prepared by reaction of the elements and was condensed fractionally, SbF_5 was distilled fractionally, and HF and DF were dried with fluorine.

In a KEL-F reactor[13] MF_5 (3 mmol; M = As, Sb) was dissolved in HF/DF (5 g). After the solution had been frozen, MF_5 (3 mmol; M = As, Sb) was added at −196 °C under an inert atmosphere (N_2). The reaction mixture was slowly allowed to warm to −60 °C. Subsequently the volatile compounds ($HF/DF/Me_3SiF$) were removed at −60 °C under dynamic vacuum. $C(OX)_3^+MF_6^-$ (X = H, D; M = As, Sb) remained as a colorless solid.

Alternatively $NaOCO_2SiMe_3$ was used as the starting material. Under identical conditions the reaction mixture was kept at −78 °C for 12 h. The alkali metal hexafluorometalates accumulate at the bottom of the reactor. After removal of the volatile components, crystalline **1**-AsF_6 formed on the walls of the vessel.

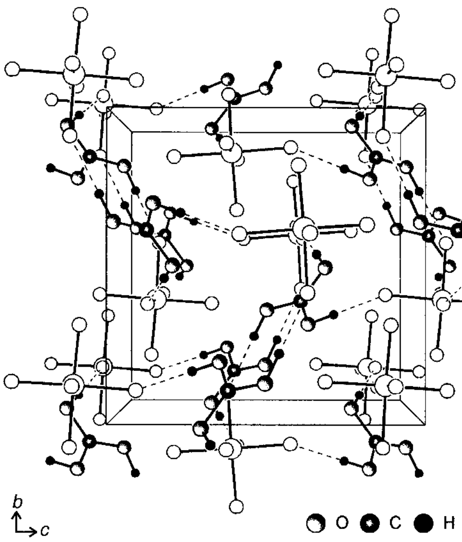

Figure 3. Section of the crystal packing of **1**-AsF_6.

Equipment: Raman: Bruker FT-Spektrometer IF66 with Raman accessory, FRA 106 Neodym-YAG-laser (λ = 1064 nm); IR: Bruker IFS 113v; NMR: Bruker DPX300; X-ray diffractometer, Nonius-Kappa CCD (1152 × 1242 pixel).

Received: September 11, 1998 [Z12403IE]
German version: *Angew. Chem.* **1999**, *111*, 752–754

Keywords: carbenium ions · carbonic acid · vibrational spectroscopy · superacidic systems · trihydroxycarbenium salts

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[10] Crystal structure investigation of **1**-AsF_6: crystals obtained from HF, cubic, space group $P2_13$ (no. 198), $a = 860.0(1)$ pm, $Z = 4$, $V = 636.0(1) \times 10^6 pm^3$; $\rho_{calcd} = 2.631 g cm^{-3}$, crystal dimensions 0.18 × 0.18 × 0.18 mm^3, $Mo_{K\alpha}$ radiation ($\lambda = 71.069$ pm), $2\theta/\omega$ scans, $2\theta_{max} = 51.0°$, $T = 173(2)$ K; 3410 measured reflections, 384 independent reflections, σ-limit 2.0; $\mu(Mo_{K\alpha}) = 5.433 mm^{-1}$, structure solution: Patterson, difference Fourier synthesis; SHELXS-86, SHELXL-93, PARST, PLATON, MISSYM, DENZO, SCALEPACK, 35 free parameters, hydrogen atoms not determined from ΔF, $R = 0.0283$, $wR = 0.0659$, $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, refinement method: full-matrix least-squares fit against F^2, min./max. residual electron density = −0.332/0.343 e Å^{-3}. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-410089.

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