Proton-donor properties of $HCCl_3$, $HSiCl_3$, and $HGeCl_3$ molecules: a quantum-chemical study

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Proton-donor properties of $HCCl_3$, $HSiCl_3$, and $HGeCl_3$ molecules were studied by quantum-chemical methods. According to calculations, the Mulliken charge of H is positive in trichloromethane and negative in the other two molecules. Trichlorogermane readily interacts with bases (B) to give the contact ion pairs $HB^+ \cdot GeCl_3^-$. Reactions of trichlorosilane with strong bases also can lead to its reorganization and the formation of contact ion pairs. In all the ion pairs, the anions are oriented to the HB^+ cations by the negatively charged Cl atoms. Owing to possible transfer of Cl^- to HB^+, this type of ion pairs can be a source of dichlorogermylene $GeCl_2$ and, probably, dichlorosilylene $SiCl_2$.

Key words: *ab initio* quantum-chemical calculations, superacids, proton-donor properties, trichlorogermane, trichlorosilane, dichlorogermylene, dichlorosilylene.

Trichlorogermane is known to possess superacidic properties in reactions with a wide range of organic bases.[1—4] In this work, we carried out *ab initio* quantum-chemical calculations of (i) the molecular and electronic structures of different isomeric forms of $HCCl_3$, $HSiCl_3$, and $HGeCl_3$ molecules and (ii) the energies of their possible transformations and compared the results obtained. We also estimated the proton-donor properties of these molecules in the gas-phase reactions with bases.

Calculation Procedure

Quantum-chemical calculations were carried out at a level of Pople's G2 approximation[5—7] with full geometry optimization using the GAUSSIAN-94 program package.[8]

Results and Discussion

Table 1 lists the results obtained in this work (the geometric parameters and electronic characteristics of the structures under study) and the published data.[9—13] The molecules $HMCl_3$ (M = C, Si, Ge) have a C_{3v} symmetry and are structurally similar. We calculated the bond lengths in these molecules (1.086, 1.468, and 1.533 Å, respectively, for M—H and 1.765, 2.032, and 2.128 Å, respectively, for M—Cl) and found that they increase as the covalent radius of the central atom M increases. The calculated Cl—M—Cl bond angles somewhat decrease in the order C > Si > Ge (111.2°, 109.6°, and 108.7°, respectively) being close to the tetrahedral angle (109.28°). The differences between the calculated and experimental

Table 1. Mulliken atomic charges (q/e), bond angles, bond lengths (d), and the energies of formation of $HMCl_3$ and MCl_2 molecules or MCl_3^- ions (E) calculated in the G2 approximation (I) and found experimentally (II)

Molecule or ion	M	q/e				E/a.u., I	Cl—M—Cl angle /deg		d(M—Cl)/Å [d(M—H)/Å]	
		Cl, I	M, I	H						
				I	II		I	II	I	II
$HMCl_3$	C	−0.159	0.248	0.229	0.14 [9]	−1417.839	111.23	110.55 [9]	1.765 [1.086]	1.762 [9] [1.073 [9]]
	Si	−0.411	1.288	−0.006	—	−1669.030	109.62	110.60 [10]	2.032 [1.468]	2.012 [10] [1.466 [10]]
	Ge	−0.566	1.743	−0.044	—	−3455.391	108.67	108.20 [10]	2.128 [1.533]	2.214 [10] [1.550 [10]]
MCl_3^-	C	−0.560	0.680	—	—	−1417.266	103.24	—	1.889	—
	Si	−0.520	0.552	—	—	−1668.491	98.13	—	2.193	—
	Ge	−0.750	1.250	—	—	−3455.391	97.29	95—97 [11]	2.309	2.261—2.289 [11]
								93.4—98.3 [12]	—	2.293—2.305 [12]
MCl_2	Si	−0.38	0.77	—	—	−1208.60	101.77	102.8 [13]	2.073	2.083 [13]
	Ge	−0.53	1.06	—	—	−2995.007	100.29	100.3 [13]	2.184	2.183 [13]

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bond lengths do not exceed 0.02 Å for Ge—H and 0.01 Å for Ge—Cl. The calculated Cl—Ge—Cl bond angle deviates from the experimental value by 0.5°.

As should be expected, the calculated Mulliken atomic charge of H atom in the $HCCl_3$ molecule is positive (0.23 e, where e is the absolute value of electron charge). The Mulliken atomic charges of hydrogen in $HSiCl_3$ and $HGeCl_3$ molecules are respectively −0.006 and −0.04 e. For the former molecule, this is consistent with the common opinion; however, the negative charge on the H atom in the covalently bonded superacid $HGeCl_3$ is in clear contradiction with the superacidic properties of this compound.

According to calculations, each Cl atom in the $HSiCl_3$ and $HGeCl_3$ molecules has a rather large negative charge of −0.41 and −0.57 e, respectively. The Si and Ge atoms in these molecules carry large positive charges (1.29 and 1.74 e, respectively). It is these atoms on which the lowest unoccupied MO (LUMO) of $HSiCl_3$ and $HGeCl_3$ molecules, which are responsible for the electrophilic properties of the Si and Ge atoms in some reactions of these compounds, are localized. The calculated energies of proton abstraction from $HCCl_3$, $HSiCl_3$, and $HGeCl_3$ molecules (Table 2) are 15.6, 14.6, and 13.4 eV, respectively (the thermochemical estimates are 16.3 eV for $HCCl_3$ and 13.6 eV for $HSiCl_3$ [14]). The calculated and experimental values for HCl coincide (14.4 eV). This comparison shows that the proton abstraction energy for $HGeCl_3$ is comparable with those of superacids. This is in agreement with the known experimental data.[1]

Similarly to the initial neutral molecules, the MCl_3^- (M = C, Si, Ge) anions have a C_{3v} symmetry. In the anions with M = Si and Ge the calculated M—Cl bond lengths are close (2.19 and 2.31 Å, respectively); this also holds for the Cl—M—Cl angles (98.1 and 97.3°, respectively). On the other hand, these values appreciably differ from the corresponding parameters of the anion with M = C (the bond lengths of 1.89 Å and the Cl—M—Cl angles of 103.2°). In the crystal, the $GeCl_3^-$ anions are usually asymmetric owing to the interaction with the counterions.[11,12,15] In this case, the Ge—Cl bond lengths are different (from 2.293 and 2.305 Å) while the Cl—Ge—Cl angles lie between 93.4 and 98.3°.[12] A comparison shows that the difference between the calculated and experimental bond lengths is somewhat larger than for the neutral molecule $HGeCl_3$ (~2%). The differences between the calculated and experimental bond angles can be as large as 2°, which seems to be due to the interaction with the counterions. In the CCl_3^- anion, the Mulliken atomic charge of carbon is positive (0.68 e) and each Cl atom carries a negative charge of −0.56 e. In the $SiCl_3^-$ anion, the Si atom has a rather large positive charge (0.55 e) while Cl atoms carry negative charges (−0.52 e each). As to the $GeCl_3^-$ anion, the Ge atom also carries a large positive charge of 1.25 e while each chlorine atom has a negative charge of −0.75 e. Owing to the electrostatic interaction, within the ion pairs the $SiCl_3^-$ and $GeCl_3^-$ anions are oriented to the corresponding cations (HB^+) by the negatively charged Cl atoms. In this case, the Cl atoms are dicoordinated while the Si and Ge atoms are tricoordinated.

Table 2. Formation energies (*E*) and proton affinity energies (*PA*) calculated in the G2 approximation

Molecule or ion	*E*/a.u.	*PA*/eV
$GeCl_3^-$	−3454.896	13.44
$GeCl_3H$	−3455.390	
$SiCl_3^-$	−1668.491	14.63
$SiCl_3H$	−1669.029	
CCl_3^-	−1417.266	15.56
CCl_3H	−1417.838	
Cl^-	−459.807	14.42

The geometric parameters found in this work for a free $GeCl_2$ molecule virtually coincide with the experimental values. The calculated Ge—Cl bond length (2.184 Å) is only 0.001 Å longer and the Cl—Ge—Cl angle (100.3°) is less than 0.1° larger than in the experiment. According to calculations for $SiCl_2$ molecule, the Si—Cl distance is 2.073 Å and the Cl—Si—Cl angle is 101.8°. Here, the differences between the experimental and theoretical values are somewhat larger, *viz*., 0.01 Å for the bond length and 1.0° for the bond angle (see Table 1). The Mulliken atomic charges of Si and Cl in $SiCl_2$ are 0.77 and −0.38 e, respectively, while those of Ge and Cl in $GeCl_2$ are 1.06 and −0.53 e (*cf.* the data listed in Ref. 14).

Weak molecular complexes formed by $SiCl_2$ (or $GeCl_2$) with hydrogen chloride are structurally similar (C_s symmetry) and have nearly equal association energies (5.2 kcal mol^{-1}). The SiCl—H and GeCl—H distances are 3.198 and 3.247 Å, respectively. In each complex, this weak bond is oriented nearly perpendicular to the plane passing through the M atom and both Cl atoms (the corresponding angle is 88.4° for M = Si and 86.0° for M = Ge). The Si—H—Cl angle is 104.7° and the Ge—H—Cl angle is 103.0°.

The enthalpies of the isomerization reactions of $HSiCl_3$ and $HGeCl_3$ are appreciably different:

$$\mathrm{HSiCl_3} \longrightarrow \mathrm{SiCl_2 \cdot HCl} \qquad (\Delta H = -0.2\ \mathrm{kcal\ mol^{-1}}),$$

$$\mathrm{HGeCl_3} \longrightarrow \mathrm{GeCl_2 \cdot HCl} \qquad (\Delta H = -21.5\ \mathrm{kcal\ mol^{-1}}).$$

It is commonly accepted that the heat of formation of a complex correlates with the height of the energy barrier that should be overcome to form the complex. Therefore, it is believed that in the case of $HSiCl_3$ the barrier to transition into the contact ion pair is much higher. Because of this, $HSiCl_3$ seems to possess the acidic properties under specific, more severe (compared to $HGeCl_3$) conditions. It should also be kept in mind that in actual practice both deprotonation and isomerization occur involving the molecule of a base, B, *via* a complex transition state.

Thus, the results of our calculations showed that the Mulliken atomic charge of H in the covalently bonded $HGeCl_3$ molecule is negative, whereas the charge of hydrogen in $HCCl_3$ is positive. The electrophilic Ge atom of $HGeCl_3$ is responsible for the acidic properties of this compound in reactions with weak bases. Owing to the extremely low proton affinity energy of $GeCl_3^-$ (13 eV), trichlorogermane behaves as a Brønsted superacid in the reactions with medium strong bases. Within the ion pair, the anion is rotated in accord with the basic properties of the negatively charged Cl atoms. This type of ion pairs can be a source of dichlorogermylene $GeCl_2$ owing to the possibility of Cl^- transfer to HB^+.

We also studied a possible structure and the relative energetics of complexes $B \cdot HGeCl_3$ and $B \cdot HCl$ (the latter were chosen for comparison) using water molecules as the base B. According to calculations, the association energy of a molecular complex $ClH \cdot OH_2$ (the Cl—H...O angle is 180°) is 13.9 kcal mol^{-1}. For the ion pair $GeCl_3^- \cdot H_3O^+$, in which all the three H atoms form a close three-point contact with three Cl atoms, this energy is 23.7 kcal mol^{-1}. In this case, the geometry of the hydroxonium ion, H_3O^+, becomes "pyramidal" (a trigonal pyramid with an H—O—H angle of 110.8°) instead of planar. The energy of addition of the second water molecule to the oxonium ion within the ion pair is 32.3 kcal mol^{-1}, which indicates that the equilibrium in the reaction

$$2\ GeGl_3^- \cdot H_3O^+ \rightleftharpoons HGeCl_3 + GeCl_3^- \cdot H_5O_2^+$$

is shifted to the right. It is noteworthy that this value is close to the formation energy of a dimeric hydroxonium ion, $H_5O_2^+$ (ΔE = 31.6 kcal mol^{-1} [16]). The magnitudes of the energy changes can of course be specific to the experimental conditions (*e.g.*, the condensed phase). However, our estimate of the ratio of the complexation energies with the first and second water molecules seems to be realistic and is consistent with the experimental data[4,15–21] which indicate that $HGeCl_3$ forms stable oxonium structures in the form of complexes with 2 : 1 stoichiometry.

Thus, trichlorogermane not only possesses superacidic properties but in many instances also behaves as a source of dichlorogermylene.[22] The results of our calculations revealed a detailed mechanism of the formation of dichlorogermylene molecule in the reactions of trichlorogermane with bases. We also showed that there are no fundamental differences between the reactions of trichlorosilane and trichlorogermane with bases and, hence, the search for experimental conditions for generation of dichlorosilylene in the liquid-phase reactions of trichlorosilane holds promise.

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