Triprotonated Hydrogen Sulfide: Pentacoordinate Sulfonium Trication SH_5^{3+} and the Search for Its Parent Pentacoordinate Oxonium Trication OH_5^{3+}**

George A. Olah,* Golam Rasul and G. K. Surya Prakash

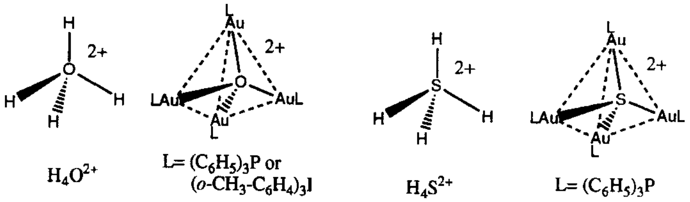
Abstract: The pentahydridosulfonium trication SH_5^{3+} was found by ab initio MP2/6-31G** and QCISD(T)/6-311G** levels of calculation to be a stable minimum with C_s symmetric structure **1**. It is isostructural with the parent pentacoordinate carbonium ion CH_5^+. Structure **1** resembles a complex between SH_3^{3+} and molecular hydrogen forming a 2e–3c bond. This structure involving a pentacoordinate sulfur atom is unprecedented. Rotation of the H_2 unit around the pseudo-C_3 axis of SH_3 is facile. The structure of SF_5^{3+} was also calculated and compared with that of **1**. In addition, our studies at the ab initio MP2/6-31G** level showed that the parent pentacoordinate oxonium trication OH_5^{3+} is not a minimum on its potential energy surface, and dissociation into OH_4^{2+} and H^+ occurs upon optimization.

Keywords
ab initio calculations · gold · isolobal relationship · sulfonium trication · superelectrophiles

Introduction

Experimental evidence for the formation of the parent oxonium dication H_4O^{2+} as an intermediate in superacids was reported by Olah et al. a decade ago.[1] Hydrogen–deuterium exchange in isotopomeric H_3O^+ species in superacids was found to occur with increasing acidity of the medium. This exchange was suggested to proceed by an associative mechanism involving H_4O^{2+} dication.[1] Like the hydronium ion, the sulfonium ion H_3S^+ was also found to undergo proton–deuterium exchange in superacids, indicating the formation of H_4S^{2+} dications.[2] Calculations showed that T_d symmetrical structures of H_4O^{2+} ion[1] and H_4S^{2+} ion[2] are the global minima on their potential energy surfaces. These dications were calculated to have considerable kinetic barriers towards deprotonation.

Using gold(I) organometallic fragment (LAu^+) as an isolobal substitute for H^+ (two fragments are considered to be isolobal if their symmetry properties, approximate energy, shape of frontier orbitals, and number of electrons are similar),[3] Schmidbaur et al. were even able to prepare dipositively charged tetrahedral gold complexes of oxygen,[4] $[\{(o\text{-}CH_3\text{-}C_6H_4)_3PAu\}_4O]^{2+}$, and sulfur,[5a] $[\{(C_6H_5)_3PAu\}_4S]^{2+}$, and determined their X-ray structures (Scheme 1). Substantial metal–metal bonding makes them stable and even isolable as crystalline salts. These gold complexes are isolobal analogues of OH_4^{2+} and SH_4^{2+}, respectively. More recently, Laguna et al.[5b] prepared and identified in solution two gold complexes of sulfur, the pentacoordinate, trigonal bipyramidal trication $[\{(C_6H_5)_3PAu\}_5S]^{3+}$ and the hexacoordinate, octahedral tetracation $[\{(C_6H_5)_3PAu\}_6S]^{4+}$. These are isolobal analogues of SH_5^{3+} and SH_6^{4+}, respectively. However, no single crystal of the penta- and hexacoordinate gold complexes derivatives could be grown.[5b] Their structural characterization has significant implications in the study of superelectrophiles.[6]



Scheme 1. Isolobal complexes of oxygen and sulfur.

In continuation of our study of gitonic onium ions (dipositive ions with proximate positive charges) we have now extended our investigations to SH_5^{3+} and found a minimum for an unprecedented pentacoordinate sulfonium trication by ab initio calculations at the correlated MP2/6-31G** and QCISD(T)/6-311G** levels of theory. We also report our ab initio calculational search for the parent oxonium *trication* OH_5^{3+}.

Calculations

The geometry optimizations and frequency calculations were performed at the MP2/6-31G** level.[7] From calculated frequencies, the optimized structures were characterized as minima, saddle-points, or transition-state structures. For the MP2/6-31G**-optimized structures further geometry optimiza-

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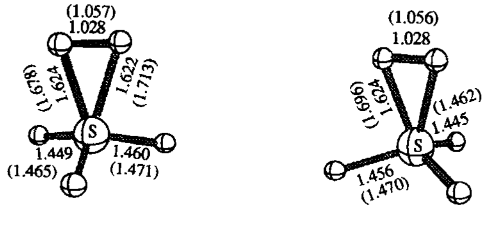
tions were carried out at the QCISD(T)/6-311G** level. For improved energy, single-point energies at the CCSD(T)/cc-pVTZ[8] level were computed on QCISD(T)/6-311G**-optimized geometries. Calculated energies are given in Table 1. Atomic charges and Löwdin[9] bond order were obtained by means of a natural bond orbital (NBO) analysis[10a] (Figure 2). Zero-point vibrational energies (ZPE) were scaled by a factor of 0.93 for MP2/6-31G**//MP2/6-31G** and 0.95 for QCISD(T)/6-311G**//QCISD(T)/6-311G** calculations. MP2/6-31G** geometrical parameters and CCSD(T)/cc-pVTZ//QCISD(T)/6-311G** + ZPE (QCISD(T)/6-311G**//QCISD(T)/6-311G**) calculated energies will be discussed throughout, unless stated otherwise.

Results and Discussion

Further protonation of OH_4^{2+} would lead to the OH_5^{3+} trication. However, we found that the entire potential energy surface of the OH_5^{3+} trication is repulsive at the ab initio MP2/6-31G** level of calculation. The trication OH_5^{3+} dissociates into OH_4^{2+} and H^+ upon optimization.

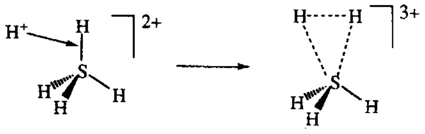
There are, however, substantial differences between the bonding nature and chemistry of oxygen and sulfur. For example, unlike oxygen the maximum coordination number of sulfur is not limited to 4, since d orbitals of sulfur may be utilized in bonding. At the MP2/6-31G** level the C_s-symmetric form **1** is a stable minimum for triprotonated hydrogen sulfide, as confirmed by frequency calculations.[10b] No other minima (e.g. D_{3h}, C_{4v} etc.) were found on the potential energy surface. Structure **1** resembles a complex between SH_3^{3+} and a hydrogen molecule forming a two-electron three-center (2e–3c) bond (Figure 1). This type of 2e–3c interaction involving sulfur atoms is unprecedented. The structure **1** is isostructural with the C_s-symmetric structure of the parent pentacoordinate carbonium ion CH_5^+, which is considered to be the parent of nonclassical carbocations.[11–13]



SH_5^{3+} **1** (C_s) SH_5^{3+} **2** (C_s) TS

Figure 1. MP2/6-31G** structures of **1** and **2** (QCISD(T)/6-311G**—level values in parentheses).

The sulfur atom in SH_4^{2+} does not undergo formal expansion of the valence octet upon protonation, since no minima of SH_5^{3+} other than **1** could be located on its potential energy surface. Structure **1**, therefore, can be viewed as being formed by insertion of a proton into one of the σ S–H bonds of SH_4^{2+} to produce a 2e–3c bond between sulfur and the hydrogen atoms (Scheme 2).



Scheme 2. Protonation of SH_4^{2+}.

The S–H bond lengths in the 2e–3c system are 1.622 and 1.624 Å at the MP2/6-31G** level. Thus, as expected, the relatively electron deficient 2e–3c S–H bonds are about 0.2 Å longer than 2e–2c S–H bonds at the same level of theory. The H–H distance in the 2e–3c bond is 1.028 Å. This is also 0.294 Å longer than that found for the hydrogen molecule at the MP2/6-31G** level of theory, and slightly shorter than that in H_2^+ (1.031 Å). The bond lengths given above for the 2e–3c system are also in agreement with the calculated Löwdin bond order (BO) of S–H (BO 0.52) and H–H (BO 0.29) in this system (Figure 2a). We also calculated the NBO charges of the ion **1** (Figure 2b). The calculated charge of sulfur atom of the trication is only +0.35*e*. The hydrogen atoms therefore bear most of the positive charge. The amount of positive charge on each of the hydrogen atoms in **1** (i.e., both those involved in 2e–3c and 2e–2c interactions) is almost equal.

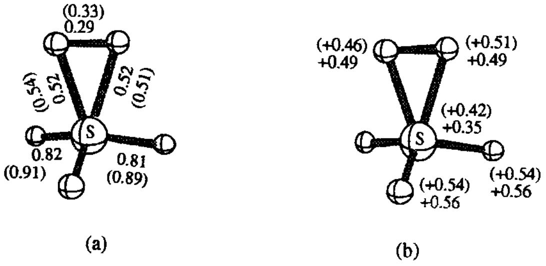


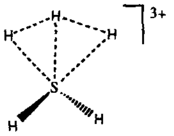
Figure 2. a) Löwdin bond orders (BO) and b) NBO charges in the ion **1** calculated at the MP2/6-31G** (QCISD(T)/6-311G**—level values in parentheses) level of theory.

Calculations were also performed for the C_s-symmetrical structure **2**, which can be formed by rotation of the H_2 unit around the pseudo-C_3 axis of SH_3 in **1** (Figure 1). At the MP2/6-31G** level the structure **2** is a transition state as it contains one imaginary frequency (i.e. NIMAG = 1) in its calculated IR spectrum and lies only 0.3 kcal mol^{-1} higher in energy than structure **1** (Table 1). At our highest level of theory (CCSD(T)/cc-pVTZ//QCISD(T)/6-311G** + ZPE) the energy difference between **1** and **2** vanished. Thus, the rotation of H_2 unit around the pseudo-C_3 axis of SH_3 of **1** via transition state **2** is facile. Calculations on CH_5^+ carbocations have also shown the rotation of the H_2 unit around the pseudo-C_3 axis of CH_3 to be facile.[12] Optimizations of the structures **1** and **2** with

Table 1. Total energies (hartree) and relative energies (kcal mol^{-1}).

	Energies (ZPE)		Relative energies	
	1	**2**	**1**	**2**
MP2/6-31G**//MP2/6-31G**	398.62310 (19.1) [a]	398.62308 (19.1) [a]	0.0	0.3
QCISD(T)/6-311G**//QCISD(T)/6-311G**	398.70536 (17.9) [b]	398.70535 (17.9) [b]	0.0	0.0
CCSD(T)/cc-pVTZ//QCISD(T)/6-311G**	398.75691	398.75691	0.0	0.0
final relative energies [c]			0.0	0.0

[a] Zero-point vibrational energies (ZPE) at MP2/6-31G**//MP2/6-31G** scaled by a factor of 0.93. [b] ZPE at QCISD(T)/6-311G**//QCISD(T)//6-311G** scaled by a factor of 0.95. [c] Final relative energies based on CCSD(T)/cc-pVTZ//QCISD(T)//6-311G** + ZPE (QCISD(T)/6-311G**//QCISD(T)//6-311G**).



SH_5^{3+}, C_{2v}

Scheme 3.

QCISD(T)/6-311G** had little effect on the geometries; the S–H and H–H bonds become slightly longer.

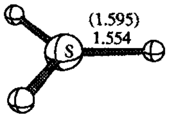
Possible intramolecular hydrogen transfer in trication **1** through a C_{2v}-type transition state (Scheme 3) was also considered. However, no such transition state could be located at the MP2/6-31G** or QCISD(T)/6-311G** levels. In contrast, a C_{2v}-type transition state for hydrogen scrambling has been calculated for CH_5^+.[12] Indeed, hydrogen scrambling in this system is extremely facile.[12]

Two possible dissociation pathways for trication **1** were considered (Table 2, Eq. (1) and (2)). As expected, both are highly exothermic; the dissociation into SH_4^{2+} and H^+ [Eq. (1)] is more exothermic by 31.6 kcal mol^{-1} than the dissociation into SH_2^{2+} and H_3^+ [Eq. (2)]. We also found that the gas-phase reaction of SH_3^{3+} trication with H_2 forming SH_5^{3+} (**1**) is highly exothermic [Eq. (3)]. Interestingly, the $SH_3^{2+\cdot}$ radical dication has been observed in the gas phase by charge-transfer mass spectrometry (CTMS).[14] As our calculations indicate that the SH_3^{3+} trication should be stable, it might be possible to observe **1** in the gas phase by the reaction of SH_3^{3+} and H_2. The calculated D_{3h} structure of SH_3^{3+} is given in Figure 3.

Table 2. Possible dissociation pathways for trication **1**.

	Eq.	ΔH (kcal mol^{-1}) [a]
SH_5^{3+} (**1**) → $SH_4^{2+} + H^+$	(1)	−257.2
SH_5^{3+} (**1**) → $SH_2^{2+} + H_3^+$	(2)	−225.6
SH_5^{3+} (**1**) → $SH_3^{3+} + H_2$	(3)	+124.4

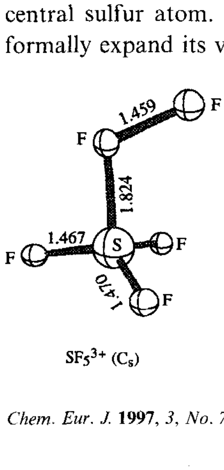
[a] At the CCSD(T)/cc-pVTZ//QCISD(T)/6-311G** + ZPE level of theory.



SH_3^{3+} (D_{3h})

Figure 3. MP2/6-31G** structure of SH_3^{3+} (QCISD(T)/6-311G**—level values in parentheses).

We also calculated the structure of SF_5^{3+} and compared it with that of **1**. Geometry optimization of SF_5^{3+} at the MP2/6-31G** level gave a C_s-symmetrical single-minimum structure (Figure 4), which resembles a complex formed by end-on coordination of F_2 with SF_3^{3+}; the S–F_2 bond is long (1.824 Å). Unlike SH_5^{3+} (**1**), SF_5^{3+} does not contain a pentacoordinate central sulfur atom. In both cases, the sulfur atom does not formally expand its valence octet. SF_5^{3+} can be described as a halonium ion type structure, that is, in $[F_3SFF]^{3+}$ the F_3S group acts as a pseudohalogen. In contrast, Cheung et al. calculated that SF_5^+ has a trigonal bipyramidal structure at the MP2(FU)/6-31G* level.[15] Five bonding electron pairs in SF_5^+ are distributed around the sulfur atom in a standard trigonal bipyramidal structure involving d orbitals.



SF_5^{3+} (C_s)

Figure 4. MP2/6-31G** structure of SF_5^{3+}

Conclusion

The present ab initio molecular orbital study shows that the parent pentacoordinate sulfonium trication SH_5^{3+} (**1**) is a minimum on its potential energy surface, although its deprotonation is highly exothermic. Our studies at the ab initio MP2/6-31G** level also show that the parent pentacoordinate oxonium trication OH_5^{3+} is not a minimum on its potential energy surface, and dissociation into OH_4^{2+} and H^+ occurs upon optimization. The structure **1** resembles a complex between SH_3^{3+} and a hydrogen molecule held together by a 2e–3c bond. This structure involving a 2e–3c bond with a pentacoordinate sulfur atom is unprecedented. The system is isostructural with that of the parent pentacoordinate carbonium ion CH_5^+. The rotation of H_2 unit around the pseudo-C_3 axis of SH_3 should be facile. We also calculated the structure of SF_5^{3+} and compared it with that of **1**. As our calculations indicate that the SH_3^{3+} trication should be stable, it might be possible to observe **1** in the gas phase by the reaction of SH_3^{3+} with H_2.

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