

The Generation of Low-Valence Sn Derivatives by Neutralization-Reionization Mass Spectrometry

Dmitri Zagorevski¹, Yang Yuan², C. Michael Greenlief²

¹ Rensselaer Polytechnic Institute, Troy, NY, ² University of Missouri-Columbia, Columbia, MO

Low-valence derivatives of Sn are rarely observed species. Formation of RSn(I) radicals as reaction intermediates has been proposed on many occasions, but only a few complexes of this type have been detected spectroscopically. The aim of the present work was to generate and characterize neutral Sn(I) derivatives in the gas phase by using neutralization-reionization mass spectrometry (NR MS). The NR MS method has been successfully applied to the generation of unstable and unknown molecules and radicals, including Si and Ge-containing complexes [1]. This technique has never been used for the characterization of Sn-derivatives. We applied the NR MS method to produce RSn (R = H, Cl, Br, CH₃, C₂H, C₆H₅) radicals from their positively charged counterparts.

NR MS and other tandem mass spectrometry experiments were performed on modified VG ZAB-2F and VG ZAB-SE mass spectrometers. Ions of interest were generated by electron impact ionization of stable Sn(IV) derivatives, mass-selected using an electromagnet and transmitted to the field-free region. Neutralization of the ions was performed in the first collision cell (CC) using NO or (CH₃)₂NH as neutralizing agents. All remaining ions were deflected from the beam of the fast moving neutrals, so that only the latter were allowed to reach the second CC where they were reionized by collisions with oxygen. The resulting ions were energy-analyzed and detected. Collision-induced dissociation of survivor ions was carried out when their yield was high enough. Experiments with isotopic ions were performed to prove the identity of the ions and the corresponding neutrals.

NR mass spectra of all RSn⁺ ions under study displayed recovery signals. Figure 1 shows the NR mass spectrum of SnC₂H⁺ ions as an example. These results indicated that the corresponding neutrals were stable in the gas phase with life-times exceeding 3 μs. CID experiments with survivor SnCl⁺ and SnCH₃⁺ ions demonstrated that the ions after the NR event were indeed those of RSn⁺. The highest yield and stability of neutral RSn was observed when nitrous oxide and dimethylamine were used for neutralization. This was consistent with the closeness of ionization energies of RSn· radicals (calculated as 6.9-7.4 eV [2]) to ionization energies of the targets (~7.2 eV). One of the reasons for the successful generation of stable neutral RSn was a favorable Franck-Condon factor. Our quantum chemical calculations using the Gaussian 98 series of programs showed that optimized equilibrium geometries of the corresponding SnR and SnR⁺ were close to each other (Table 1).

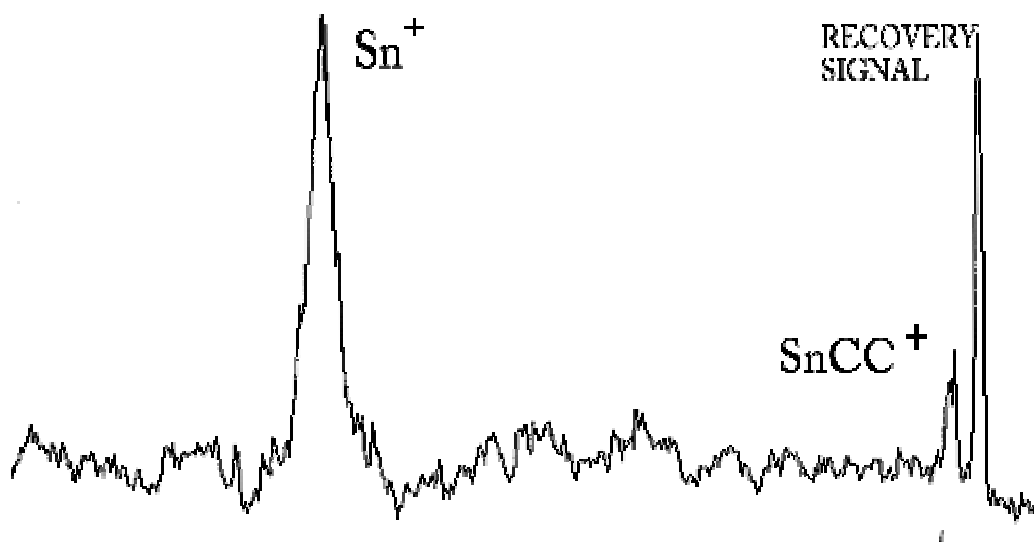


Figure 1. Neutralization-reionization mass spectrum (NO/O₂) of ¹²⁰SnC₂H⁺ ions.

NR mass spectra of all studied RSn⁺ ions displayed peak(s) due to Sn⁺ ions. The absence of R⁺ ions (except for R = C₆H₅) indicated that the contribution from the dissociation of neutral RSn to the NR mass spectra was relatively small.

In conclusion, NR MS is a convenient method for the generation of otherwise unstable low-valence derivatives of Sn. Our results confirmed the intrinsic stability of known or theoretically predicted RSn radicals (R = H, Cl, Br, CH₃). The results for SnC₂H⁺ and SnC₆H₅⁺ ions provided the first experimental evidence for the stability of SnC₂H[•] and SnC₆H₅[•] neutrals.

Table 1. Selected optimized geometrical parameters (bond lengths in Å) for RSn ions and neutrals.

Ion/neutral	d(C-Sn)	d(C-C) ^{a)}	d(C-H) ^{a)}	Other
C ₆ H ₅ Sn	2.270	1.409	1.087	Sn-phenyl 118.7° ^{b)}
C ₆ H ₅ Sn ⁺	2.322	1.412	1.086	Sn-phenyl 117.0° ^{b)}
C ₂ HSn	2.037	1.236	1.068	Sn-C-C 180°
C ₂ HSn ⁺	2.000	1.236	1.075	Sn-C-C 180°
CH ₃ Sn	2.401	-	1.089	Sn-C-H 102.2° ^{a)}
CH ₃ Sn ⁺	2.480	-	1.092	Sn-C-H 100.5° ^{a)}

^{a)} average values; ^{b)} dihedral angle

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