**Experimental and theoretical study of the elementary reaction of tin with oxygen: gas-phase formation of SnO**

**BORING I’m thinking…**

Iakov A. Medvedkov,1 Anatoliy A. Nikolayev,2 Shane Goettl,1 Zhenghai Yang,1Alexander M. Mebel,3\* Ralf I. Kaiser1\*

1 *Department of Chemistry, University of Hawai‘i at Manoa, Honolulu, HI 96822, USA*

2 Samara National Research University, Samara 443086, Russia

3 Department of Chemistry and Biochemistry, Florida International University, Miami, Florida 33199, USA

Corresponding to: ralfk@hawaii.edu; mebela@fiu.edu

**Abstract**

200  words

**1. INTRODUCTION**

     Since the exploitation of the main group XIV element tin (Sn) merged with the transition metal copper (Cu) in bronze alloys more than 5,000 years ago,1 the preparation and properties of subvalent tin (II) compounds together with their isovalent carbon (C), silicon (Si), and germanium (Ge) counterparts have intrigued the computational chemistry, physical inorganic, and preparative synthetic communities from the perspectives of electronic structure theory and chemical bonding.2 From carbon to tin, the electronic structure of the dihydrides transforms noticeably (Scheme 1, **1-12**). Whereas for the lightest main group XIV element carbon, the divalent hydride methylene (CH2, X3B1) has a triplet electronic ground state and a singlet-triplet splitting to the a1A1 state of 36 to 38 kJ mol–1,3,4 all higher homologues silylene (SiH2), germylene (GeH2), and stannylene (SnH2) hold an X1A1 electronic ground state. The singlet-triplet splitting to the a3B1 state increases from 80–88 kJ mol–1 in silylene (SiH2) 5–11 via 100–105 kJ mol–1 in germylene (GeH2) 12 and 98–111 kJ mol–1 12,13 in stannylene (SnH2) as the period increases. This trend can be rationalized in terms of discrete sizes of the valence orbitals of carbon, silicon, germanium, and tin; the enhanced size of the valence orbitals of silicon, germanium, and tin compared to carbon results in an ineffective hybridization of the s and p orbitals in silicon, germanium, and tin; this is accompanied by the stabilization of the singlet versus triplet state in silylene, germylene, and stannylene. This finding correlates nicely with the reduction of the H-E-H angles (E = C, Si, Ge, Sn) in the electronic ground states, which are reduced from 129.8° (**5**, CH2, X3B1) via 93.4° (**2**, SiH2, X1A1) to 92.3° (**3**, GeH2, X1A1) and 92.4° (**4**, SnH2, X1A1) (Scheme 1)14,15. The diminished reactivity of stannylene (SnH2) 16 compared to their isovalent methylene (CH2),17–21 silylene (SiH2),22–24 and germylene (GeH2) analogues 25 culmi­nated in the preparative synthesis of subvalent tin (II) com­pounds such as  Sn2[(Me3Si)2CH]26 and Sn[N(SiMe3)]2.27

The mounting attention in the (in)organic tin (II) chemistry and industrial applications of tin (II) oxide (SnO) in conjunction with indium tin oxide (ITO) on touchscreens and thin film transistors (TFT)28,29 revitalized widespread research in the electronic structure and chemical bonding of binary oxides of main group XIV elements. In gas-phase carbon monoxide (CO), two and one -bond generate a carbon-oxygen triple bond.30,31 Whereas carbon monoxide is a gas at 293 K, gas-phase silicon monoxide (SiO), is unstable and disproportionates to amorphous silicon and silicon dioxide (SiO2).32,33 In the diatomic oxides, the bond lengths increase from carbon via silicon and germanium to tin from 112.8 pm via 151.2 pm and 161.7 pm to 183.3 pm.34 The electronegativity difference between the main group XIV element and oxygen rises from 1.00 in carbon monoxide (CO) to 1.78 in tin monoxide (SnO) on the Pauling scale suggesting an enhanced ionic character in the tin – oxygen bond compared to the carbon – oxygen bond. Also, within main group XIV, the +II oxidation state becomes increasingly stable as demonstrated by the stability of commercially available tin(II) and tin(IV) compounds such as tin(II) chlorideand tin(IV) sulfide. Nevertheless, tin(IV) is still considered to be more stable than tin(II); as such, tin monoxide (SnO) emerged as a reduction agent that can be oxidized easily to tin dioxide (SnO2). 35 Chlorides and organic compounds such as tin tetrachloride (SnCl4), tetramethyltin ((CH3)4Sn), and dimethyldichlorotin ((CH3)2SnCl2) are used as precursors for the gas-phase synthesis of tin dioxide. These precursors decompose36–38 into atomic tin, which also makes studying the reaction of tin plus molecular oxygen (O2) an indispensable step to untangle the reaction mechanism during the synthesis of tin dioxide. Previously, the kinetics of the reaction of atomic tin with molecular oxygen were studied at high temperatures of 1300 to 2600 K using a shock tube equipped for atomic resonance absorption spectroscopy (ARAS),39,40 in a fast-flow reactor with laser-induced fluorescence (LIF) over the wide temperature range 380 to 1840 K.41, and by flash photolysis absorption spectroscopy at 295K.42–44 Studies demonstrate that the reaction is spin-allowed the main products are tin monoxide (SnO, X1Σ+) and atomic O(3P), while no explanations were offered for the difference in the measured rate coefficients (Table 1).

     However, whereas tin dioxide (SnO2) has been successfully synthesized in the gas phase exploiting flame spray pyrolysis and droplet combustion techniques,45 no route has been developed to prepare divalent tin monoxide (SnO, **12**) in a directed synthesis. Here, we report the first gas-phase preparation of tin monoxide (SnO, **12**, X1+) through the bimolecular reaction of ground state tin atoms (Sn; 3Pj) with molecular oxygen (O2; X3) utilizing the crossed molecular beams technique.46,47 An elucidation of elementary reactions at the microscopic level in tandem with electronic structure calculations affords remarkable insights into the intimate reaction dynamics through which highly reactive subvalent oxides like tin oxide (SnO, **12**, X1+) can be generated via a single collision event be­tween the atomic tin and a prototype oxidant (O2; X3) un­der single-collision conditions in the gas phase through non-adiabatic reaction dynamics. This reaction is also of fundamental importance to the reaction dynamics community as a benchmark of triatomic systems involving the ‘heavy’ main group XIV element tin, which has been elusive until now, and the comparison with the isovalent Si – O2 48and Ge – O2 49systems explored previously.

**2. METHODOLOGY**

    The crossed molecular beams approach47,50–56 represents a versatile experimental technique to eluci­date the reaction dynamics of bimolecular reactions of fundamental importance to, e.g., combustion chemistry, 51 astrochemistry,47 planetary sciences, 57,58 catalysis, 59 and material sciences.60 After all, the complex networks of chemical processes occurring in, e.g., combustion flames and extraterrestrial environments consist of a series of elementary reactions, most of which are bimolecular collisions between an atom or radical and a closed shell species. Consequently, a detailed experimental knowledge of the elementary processes involved at a fundamental microscopic level is imperative to assess the nature of the primary reaction products. Here, experiments under single collision conditions are vital to achieve this goal since in a binary collision involving two reagents formed in separate side chambers, reactant 1 (here: atomic tin) only reacts with a single molecule of reactant two (here: molecular oxygen); successive reactions of the primary products are eliminated. This prerequisite assures that solely primary reaction products are identified. Most importantly, in contrast to bulk experiments, where the reactants are mixed, the chief benefit of a crossed beam experiment is the ability to generate the reactants in separate, supersonic beams, and atomic tin will only collide (and sometimes react) with the oxygen molecule of a second beam at a specific collision energy and crossing angle.

     To monitor the product(s) formed under single collision conditions, our setup implemented a triply differentially pumped, universal quadrupole mass spectrometric detector (QMS) coupled to an electron impact ionizer operating at extreme ultrahigh vacuum conditions of typically high 10–12 Torr. Here, any reactively species scattered from the collision center after a single collision event has taken place can be ionized in the electron impact ionizer operated with 80 eV electrons at a current of 2 mA; therefore, it is feasible to verify the mass (and the gross formula) of all the products of a bimolecular reaction by varying the mass-to-charge ratio, *m/z*, in the mass filter. Considering that the detector is rotatable within the plane defined by both beams, this detection system allows mapping out the angular and velocity distributions of the scattered products. Measuring the time-of-flight (TOF) of the products from the interaction region over a defined flight length affords the elucidation of the product translational energy and angular distributions in the center-of-mass reference frame. This provides knowledge into the nature of the chemical reaction (direct vs indirect), intermediates involved, the reaction product(s), branching ratios, and in some cases the preferential rotational axis of the fragmenting complex(es) and the disposal of excess energy into the products’ internal degrees of freedom as a function of scattering angle and collision energy (Results Section).

**3. EXPERIMENTAL**

The gas-phase reaction of atomic tin (Sn; 3Pj) with molecular oxygen (O2; X3) was carried out under single-collision conditions using the crossed molecular beams machine.46,61 The experimental setup, data acquisition, and data processing are described elsewhere in detail.62–64 Briefly, the reactant atomic tin (Sn, 3Pj) was generated *in situ* in the primary source chamber by laser ablation (3mJ, 266nm, 30 Hz; Quanta-Ray) from a rotating tin rod (99.98% Sn, Alfa Aesar) and seeding the ablated atoms in a pulsed argon beam (Ar, 99.9999%; Airgas) that was released from a piezoelectric valve operating at 60 Hz and a backing pressure of 4 atm. All five most abundant isotopes of tin 65 were detected in the beam with the signal ratios matching their natural abundance (Table 2). The atomic tin beam was skimmed and velocity selected using a four-slot chopper wheel; this achieved a peak velocity *vp* = 631 ± 22 m s–1 and speed ratio S = 8.5 ± 0.6. Neat oxygen gas (550 Torr, O2, 99.998%; Matheson) was used as a precursor to produce the ‘reactant two’ supersonic molecular oxygen beam (60 Hz, *vp* = 776 ± 20 m s–1, S = 15.6 ± 1.0) in the secondary source chamber. Both molecular beams intersected at an angle of 90° in the scattering chamber at a mean collision energy of EC = 13 ± 1 kJ mol–1. The reactively scattered products were ionized by electron ionization at 80eV (2mA) at the entrance of the rotatable detector, filtered according to *m/z*  by the QMS (Extrel, QC 150; 1.2 MHz), and detected using a Daly-type particle ion counter.66 Angularly resolved time-of-flight (TOF) spectra were recorded at discrete laboratory angles in 2.5° steps. Operating the laser at half frequency of the pulsed valves and sufficient length of the recorded TOFs allowed an instant background subtraction (“laser-on” minus “laser-off”) during the TOF recording.

To gain information on the reaction dynamics, TOF spectra and the laboratory angular distribution (LAD) were transformed from the laboratory to the center-of-mass frame by a forward-convolution routine.67,68 This approach uses initially a trial angular flux T(θ) and translational energy P(ET) distributions in the center-of-mass (CM) frame to simulate the TOFs and LAD (laboratory data). CM functions were iteratively varied until the best fit of the TOF spectra and LAD was achieved. Together the CM functions constitute the reactive differential cross sections I(θ, u) ∼ P(u) × T(θ), where u – the CM velocity, θ – angle in the CM system. The reactive differential cross sections can be represented as a flux contour map that depicts the probability of the products to scatter at the specific angle (θ) with the specific kinetic energy (u).

**4. COMPUTATIONAL**

**XXX**

**5. RESULTS**

**Laboratory frame**

The ratios of the natural isotope abundances of tin 116Sn, 117Sn, 118Sn, 119Sn, 120Sn, 122Sn, and 124Sn are 14.5, 7.7, 24.2, 8.6, 32.6, 4.6 and 5.8%, respectively. Therefore, the reactive scattering signal for tin monoxide (SnO) was initially monitored in the range of *m/z* 132 – 141. The ratio of the collected signal of tin monoxide at the center-of-mass angle nicely matches the prediction from the natural abundance of tin isotopes (Figure 2). Non-zero signals at *m/z* = 137 and 139 arise from the presence of 18O isotopes. These raw data alone demonstrate a single reaction channel via the emission of atomic oxygen (16 amu) and formation of tin monoxide (116Sn16O+, *m/z* = 132; 117Sn16O+, *m/z* = 133; 118Sn16O+, *m/z* = 134; 119Sn16O+, *m/z* = 135; 120Sn16O+, *m/z* = 136; 122Sn16O+, *m/z* = 138; 124Sn16O+, *m/z* = 140) in the reaction of atomic tin with molecular oxygen. The corresponding TOF spectra were collected at the best signal-to-noise ratio at *m/z* = 136 (Figure 3a) and were then normalized to the signal at CM angle to obtain the laboratory angular distribution (LAD). More than 2.5 × 106 TOF spectra were recorded between 8.75° ≤ Θ ≤ 58.75° with the tin beam defined as Θ = 0° direction. The LAD is rather wide, starts at 53.75°, and extends beyond the range of the rotating detector at small angles (less than 8.75°). The TOF spectra are broad from at least 700 to 1500 μs and peak between 750 and 900 μs. These findings propose that the tin monoxide products were formed via indirect scattering dynamics through complex formation involving SnO2 intermediates. 46,50,57

**Center-of-Mass Frame**

To further illuminate the underlying reaction mechanism(s) accompanied by the potential involvement of intersystem crossing (ISC), excited state surfaces, and non-adiabatic reaction dynamics, a transformation of the laboratory data from the laboratory reference frame into the center-of-mass reference frame is accomplished using single channel fit of the laboratory data and reaction (1):

120Sn(3Pj) + 16O2(X3) → 120Sn16O(X1+) + 16O(3P). (1)

The best-fit CM functions are depicted in Figures 4a and b. The error ranges of the P(ET) and T(θ) functions are determined within the 1σ limits of the corresponding laboratory angular distribution and beam parameters (beam spreads and beam velocities) while maintaining a good fit of the laboratory TOF spectra and LAD. The translational energy flux distribution P(ET) (Figure 4a) contains valuable information about reaction dynamics and thermodynamics. The derived P(ET) distributions exhibit a maximum translational energy release (Emax) of 92 ± 13 kJ mol–1. Energy conservation dictates that for those molecules born without internal excitation, Emax is the sum of the collision energy (EC) and the reaction energy. Taking into account the collision energy of 13 ± 1 kJ mol–1, the reaction energy was determined to be exoergic by 79 ± 14 kJ mol–1. Moreover, the P(ET) distribution peaks at 20 ± 3 kJ mol–1, indicating a tight exit transition state yielding tin monoxide and a ground state oxygen atom.69 Thermodynamic analysis of our experimental results proves the observation of reaction (1) with stated electronic and spin-orbit levels. In the case of the presence of only the Sn(3P0) in the beam reaction energy would be –36 kJ mol–1,70 while reaction energy calculated for the Sn(3P2) provides an excellent match (–76 kJ mol–1) with the experimental data. Sn(3P0) and Sn(3P1) are also present in the beam but masked in the lower energy section of the CM translational energy distribution (Figure 3a). Production of higher energetic species SnO(a3Σ+) or O(1D) drives the reaction endoergic to +208 or +151 kJ mol–1, respectively. These reactions are closed under our experimental conditions with Ec = 13 ± 1 kJ mol–1. The average translational energy of the products was derived to be 31 ± 5 kJ mol–1, suggesting that 34 ± 10% of the total available energy is channeled into the translational degrees of freedom of the products, which usually implies that the reaction mechanism proceeds through the formation of a covalently bound intermediate.46,50,57 The center-of-mass angular distribution T(θ) can provide additional information about the reaction dynamics (Figure 4b). The ‘flat’ T(θ) reveals that products after a collision are scattered in all directions with equal probability (isotropic scattering). The forward-backward symmetry and intensity distribution also propose indirect scattering dynamics via long-lived (longer than their rotational periods) SnO2 complex(es).69 Foresaid findings are also enclosed in the flux contour map (Figure 4c), which depicts an overall image of the reaction scattering process.

**I STOPPED HERE – needs theory results…..**

**6. DISCUSSION**

Now we combine our experimental results with electronic structure and statistical calculations to unlock the underlying chemical dynamics and reaction mechanism(s) of atomic tin oxidation in the gas phase.

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