# CHEMILUMINESCENT REACTIONS OF Sn<sub>2</sub>, Ge<sub>2</sub> AND Si<sub>2</sub> WITH O<sub>2</sub>

J.M. PARSON, J.H. WANG, C.C. FANG and B.S. CHEONG

Chemistry Department, The Ohio State University, Columbus, OH 43210, USA

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Chemiluminescence observed in a beam-gas study of group 14 elements with  $O_2$  is attributed to efficient reactions of the group 14 dimers. Comparisons are presented with chemiluminescent reactions of the atoms with  $N_2O$  and  $NO_2$ .

### 1. Introduction

Emission of electronically excited PbO, SnO, and GeO formed in reactions of lead, tin, and germanium vapors with molecular oxygen has been previously observed in flow systems [1–4]. No mechanism, however, has been clearly established as a major source of this emission. Insufficient energy is released in reactions of the ground state atoms with  $O_2$  to populate any electronically excited states. Hence proposals have been made of multistep pathways such as [4]

$$M + O_2 \rightarrow MO + O, \qquad (1a)$$

$$M + O \xrightarrow{Ar} MO^*$$
, (1b)

where M is Pb, Sn or Ge. Reaction (1a) serves to generate O atoms, and energetics require that M be electronically excited in the case of M=Pb. However, no direct confirmation of these pathways is available. By studying these reactions with molecular beams we have been able to identify a single-step mechanism for populating the electronically excited states which involves reaction of dimers with  $O_2$  to form with high probability one electronically excited and one ground state product,

$$M_2 + O_2 \rightarrow MO^* + MO, \qquad (2)$$

where M is Sn, Ge, or Si. The results are consistent with the known MO bond strengths and previously assigned excited electronic states. Comparisons are made with reactions of these atoms with  $N_2O$  and  $NO_2$ , where considerable information is available on the chemiluminescent mechanisms [1-3,5,6].

#### 2. Experimental arrangement

Group 14 elements were vaporized in a high temperature beam source in a molecular beam apparatus which has been described previously [7]. The vapors were collimated upon entering a separately pumped chamber filled with a pressure of O<sub>2</sub> of typically 10<sup>-4</sup> Torr. Chemiluminescence (CL) was viewed at 90° to the beam either through an interference filter followed by an EMI 9789OB tube, or through a 3/4 m Spex monochromator with a spectral bandpass of 3 nm, followed by an RCA C31034 PM tube. The interference filter combination was used with time-of-flight (TOF) sampling of the CL signal following the formation of 26 µs (fwhm) pulses of the beam via rotation of a slotted wheel in the beam path. The monochromator was scanned to obtain low resolution emission spectra, which were corrected for spectral response using calibrated deuterium and quartz-halogen lamps. For comparison with previous reports of CL in reactions of Sn, Ge, and Si with N<sub>2</sub>O and NO<sub>2</sub> under multiple-collision conditions [1-3,5,6] and of Si under singlecollision conditions [5,6], these gases were substituted for  $O_2$  in both the TOF measurements and the spectral scans.

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### 3. Results and analysis

Chemiluminescence was observed from the well known lowest A  $^{1}\Pi$  and b  $^{3}\Pi$  states [8] of SnO, GeO and SiO when O2 was used as an oxidizing gas. These transitions connect to the ground  $\Sigma^+$  states. The emission intensity in each case rose linearly with the O<sub>2</sub> pressure at low pressures, indicating reactions which are first order in  $O_2$ . The emission intensity for M=Ge and Sn was found to be second order in M, which was monitored by an electrodeless discharge lamp. The consequent first-order dependence on M<sub>2</sub> is consistent with the TOF results discussed below, which established M<sub>2</sub> as the reactant. A discharge lamp was not available for monitoring Si. Fig. la displays the SnO spectrum, which did not indicate emission from the lower a  ${}^{3}\Sigma^{+}$  state. Ge shows the same pattern of behavior. In contrast, SnO and GeO spectra obtained under multiple-collision conditions in flames also contain emission from the  ${}^{3}\Sigma^{+}$ state to the ground state [1,2]. For SiO weaker emission is also seen in fig. 2 in the region 350-450 nm. which can be assigned to transitions from higher triplet states (f <sup>3</sup> $\Pi$  and c <sup>3</sup> $\Sigma$ <sup>+</sup>) [8] to the lowest <sup>3</sup> $\Pi$ state. No PbO emission was observed under our conditions.

With N<sub>2</sub>O as an oxidizing gas, spectra are dominated by the  ${}^{3}\Pi - {}^{1}\Sigma^{+}$  transition for SnO (see fig. 1b), GeO, and SiO. Signal to noise in the  ${}^{1}\Pi$  and  ${}^{3}\Sigma^{+}$ 



Fig. 1. Chemiluminescent spectra of (a)  $Sn_2+O_2$ , (b)  $Sn+N_2O$  and (c)  $Sn+NO_2$ . Origins of the A-X, b-X and a-X systems of SnO are shown. The spectra are relative photon counts corrected for the spectral response but not normalized with respect to each other.



Fig. 2. Chemiluminescent spectrum of  $Si_2+O_2$  at two levels of sensitivity. Origins of the A-X, b-X, f-b and c-b systems of SiO are shown. The photon count scale in the lower panel has been expanded by 20 times.

emission regions was insufficient to ascertain the presence of these states, which have been noted under multiple-collision conditions [1-3] and in SiO under single-collision conditions [5,6]. We estimate upper limits for ' $\Pi$  and  ${}^{3}\Sigma^{+}$  emission at 10% of  ${}^{3}\Pi$  emission.  ${}^{3}\Pi$  formation can be explained by a spin-conserving reaction,

$$M({}^{3}P) + N_{2}O({}^{1}\Sigma^{+}) \rightarrow MO({}^{3}\Pi) + N_{2}({}^{1}\Sigma_{g}^{+}), \quad (3)$$

and this reaction has been postulated to explain a high photon yield in the  $Sn + N_2O$  reaction [3].

One might be tempted to attribute the absence of  ${}^{3}\Sigma^{+}-{}^{1}\Sigma^{+}$  emission in both O<sub>2</sub> and N<sub>2</sub>O reactions to much longer radiative lifetimes of the  ${}^{3}\Sigma^{+}$  states compared to the  ${}^{3}\Pi$  states, as laser-induced fluorescence studies of PbO indicate this trend in the lifetimes [9]. However, NO<sub>2</sub> in reacting with Sn and Ge gives much stronger emission from the  ${}^{3}\Sigma^{+}$  states than the  ${}^{3}\Pi$  states. This is shown in fig. 1c for SnO and can be attributed to the reaction

$$M(^{3}P) + NO_{2}(^{2}A_{1}) \rightarrow MO(^{3}\Sigma^{+}) + NO(^{2}\Pi)$$
. (4)

The dominance of the  ${}^{3}\Sigma^{+}$  states can be understood based on reaction (4) being energetically allowed, while formation of the  ${}^{3}\Pi$  state is endoergic. For the Si reaction with NO<sub>2</sub>,  ${}^{3}\Pi - {}^{1}\Sigma^{+}$  emission dominates, but there are indications that the  ${}^{3}\Sigma^{+}$  radiative lifetime may be much longer because of less coupling to the singlet-singlet emission system [5,10], which would imply that most of the  ${}^{3}\Sigma^{+}$  product flies out of the region viewed before it radiates. Unfortunately, quantitative comparisons on the relative rates of  ${}^{3}\Pi$  and  ${}^{3}\Sigma^{+}$  formation are not possible without radiative lifetime measurements.

In considering possible mechanisms for the O<sub>2</sub> CL reactions, the contributions of metastable atomic states and dimers were considered since CL from <sup>3</sup>P ground state reaction is energetically forbidden. Table 1 gives excergicities calculated for reaction of the thermally populated <sup>1</sup>D states and  $T_e$  values for the observed MO electronic states. Also shown are the ratios of dimer to monomer populations in the beams that were employed. It is clear that only the dimer reactions provide sufficient energy to populate the observed states, even if typical collision energies of  $\approx 1000 \text{ cm}^{-1}$  are added to the energy available. Also understandable is the failure to observe PbO CL under our conditions, which give a very small dimer to monomer ratio as well as insufficient energy for forming the lowest excited PbO state. TOF studies of the Sn<sub>2</sub> and Ge<sub>2</sub> reactions with O<sub>2</sub> provide further confirmation of reaction (2). Fig. 3 shows the total CL signal as a function of the flight time of Sn<sub>2</sub> over the 19.8 cm from the beam source. In order to interpret this TOF spectrum one must know the velocity distributions of the Sn and Sn<sub>2</sub> components in the beam. The Sn velocity distribution was measured by exciting fluorescence of the beam with an electrodeless discharge lamp. By comparing this distribution to a Maxwell–Boltzmann form, we determined an oven temperature which was close to the one obtained directly by optical pyrometry. This indicates that acceleration of the beam due to noneffusive flow was minimal. The temperature determined was then used to calculate the  $Sn_2$  velocity distribution, which was convoluted with the  $O_2$  velocity distribution using a line-of-centers model [15] for the cross section as a function of collision energy  $E_{T}$ ,

$$\sigma \sim 1 - V/E_{\rm T}$$
 .

The predicted TOF spectrum shown in fig. 3 represents a non-linear least-squares fit with a value for the energy barrier V of 9.0 kJ mol<sup>-1</sup>. The Ge<sub>2</sub> reaction with O<sub>2</sub> was fit in a similar fashion with V=4.9 kJ mol<sup>-1</sup>. In contrast, the Sn and Ge reactions with N<sub>2</sub>O and NO<sub>2</sub> gave TOF peaks at shorter times, which can be fit with the line-of-centers cross section but using the atom velocity distributions.

An absolute cross section for reaction (2) to form  $\text{SnO}(^{1,3}\Pi)$  can be estimated since the radiative lifetimes of these states are likely to be short enough to allow negligible loss of light collection in the TOF apparatus due to molecules flying out the region viewed before radiating. Using laser-induced fluorescence of the b-X transition, Clyne and Heaven [16] found a radiative lifetime of only 580 ns for v=14 of the <sup>3</sup> $\Pi$  state and 160 ns for v=1 of the <sup>1</sup> $\Pi$ 

Table I

Possible reactions for populating excited MO states and the dimer-to-monomer beam ratio at the temperatures given. Energies are in  $cm^{-1}$ 

Reaction	$-\Delta H_0^{(-a)}$	T <sub>c</sub>	$M_2/M$	<i>Т</i> <sub>м</sub> ( <b>К</b> )
 $Si(^{1}D) + O_{2} \rightarrow SiO + O$	31700		0.01 <sup>d</sup> )	2200
$Si_2 + O_2 \rightarrow 2SiO$	66100	b <sup>3</sup> П. 33947 А <sup>1</sup> П, 42835 f <sup>3</sup> П, 59261		
$Ge(^{1}D) + O_{2} \rightarrow GeO + O$	20500		0.0 <b>4</b> °)	1900
$Ge_2 + O_2 \rightarrow 2GeO$	45400	b <sup>3</sup> П, 32132 А <sup>1</sup> П, 37767		
$Sn(^{1}D)+O_{2}\rightarrow SnO+O$	11600		0.005 f)	1800
$Sn_2 + O_2 \rightarrow 2SnO$	31300	b ³П₁, 24890 А <sup>।</sup> П, 29624		
$Pb_2 + O_2 \rightarrow 2PbO$	13900 b)	$a^{3}\Sigma^{+}$ , 16025 <sup>c)</sup>	0.0008 g)	1280

<sup>a)</sup> Bond strengths were taken from ref. [8].

<sup>b</sup>) Reactions of thermally populated metastable Pb states are endoergic.

<sup>c)</sup> No emission from this state was observed.

<sup>d)</sup> Ref. [11]. <sup>e)</sup> Ref. [12]. <sup>f)</sup> Ref. [13]. <sup>g)</sup> Ref. [14].



Fig. 3. TOF spectrum of  $Sn_2 + O_2$ . Relative photon count versus  $Sn_2$  flight time is shown by the points. The smooth curve gives the calculated spectrum based on a line-of-centers cross section.

state. Although lower vibrational levels of the  ${}^{3}\Pi$  state are expected to have longer lifetimes, we assume that they are shorter than the characteristic time for travel out of the region viewed of  $\approx 10 \ \mu$ s. The cross section can be estimated by comparing the total light emission with that observed in reactions of Sn with  $F_{2}$  and  $N_{2}O$ , where cross sections are available. The reaction

$$\operatorname{Sn}({}^{3}\mathrm{P}) + \mathrm{F}_{2} \to \operatorname{SnF}({}^{2}\Sigma^{+}) + \mathrm{F}$$
(5)

has been found to have a cross section of  $\approx 2.6 \text{ Å}^2$  [17]. Using the Sn dimer to monomer ratio and the relative integrated photon count, we obtain an estimate of  $\approx 21 \text{ Å}^2$  for CL in reaction (2). Likewise, the absolute cross section for reaction (3) can be estimated from Felder and Fontijn's [3] photon yield for the <sup>3</sup>II state of  $0.15\pm0.09$  and the total rate of Sn reaction with N<sub>2</sub>O to form all products. The resultant estimate for the O<sub>2</sub> cross section is 18 Å<sup>2</sup>. The agreement between the two values is certainly acceptable in light of the 50% uncertainty in the F<sub>2</sub> cross section and the error in extrapolating the N<sub>2</sub>O photon yield to low pressures. We note that this large CL

cross section is consistent with the small energy barrier obtained from the TOF studies.

## 4. Discussion

Many reactions which are energetic enough to populate electronically excited products yield only a small fraction of products in radiative states. Notable exceptions have been explained in terms of constraints provided by conservation of spin or orbital symmetry. Because of the facility of non-adiabatic transitions, the overall symmetry correlation from reactants to products does not appear to be as reliable a guide as one suggested by its success in predicting reactive channels in light systems [18]. Full explanations of electronic state partitioning will require large scale ab initio calculations of the regions of intersection and avoided crossing of potential energy surfaces. Experiments which show strong propensity for excited product formation provide important examples for theoretical investigation.

The reactions of group 14 dimers with  $O_2$  appear to produce one excited product with high efficiency and to proceed with only small energy barriers. Also noteworthy is the selectivity of the electronic state branching:  ${}^{1}\Pi$  and  ${}^{3}\Pi$  emission is observed, but not emission from the lower  ${}^{3}\Sigma^{+}$  state. N<sub>2</sub>O reactions likewise discriminate against a  ${}^{3}\Sigma^{+}$  formation, which we observed only in the NO<sub>2</sub> reactions with Sn and Ge. If we consider adiabatic correlation of reactant and product states so as to conserve the overall orbital and spin symmetries, we do not expect the observed outcomes in electronic branching. The ground state of M<sub>2</sub>, which has  ${}^{3}\Sigma_{g}^{-}$  symmetry [8], combines with the  ${}^{3}\Sigma_{g}^{-}$  state of O<sub>2</sub> to correlate with one  $MO(a^{3}\Sigma^{+}) + MO(X^{1}\Sigma^{+})$  if a triplet surface is followed, or two  $X^{1}\Sigma^{+}$  products on a singlet surface. This result holds whether the system geometry is unconstrained or restricted to collinear or planar geometries. In reaction with N<sub>2</sub>O the ground state of M, with  ${}^{3}P_{g}$  symmetry, does correlate exclusively with the observed  ${}^{3}\Pi$  state of MO, but only if the system is constrained to a collinear geometry. Apparently these systems can be highly selective even when nonadiabatic processes are required. A similar situation arises in the reaction of  $Sn(^{1}D)$  with  $F_{2}$  to give excited SnF( ${}^{2}\Sigma^{+}$ ) with high efficiency [19]. The selectivity could be explained by noting the orbital symmetry of the unpaired electron of Sn after the first electron bonds to F. For M<sub>2</sub> and MO, the generalized valence bond (GVB) approach [20,21] gives a qualitative picture of the orbital geometries. The valence orbitals in the  ${}^{3}\Sigma_{\rho}^{-}$  ground state of M<sub>2</sub> are represented in fig. 4 where the three non-bonding electrons on each atom are either unpaired in p orbitals or paired in sp hybrid "lobe" orbitals. We note that reaction with O<sub>2</sub>, which has the valence orbital geometry shown in fig. 4, leads efficiently to the  $^{1}\Pi$ or <sup>3</sup> $\Pi$  state of MO, which unlike the <sup>1</sup> $\Sigma$ <sup>+</sup> or <sup>3</sup> $\Sigma$ <sup>+</sup> state has a lobe orbital involved in bonding. We speculate that this occurs because one of the M atoms in M<sub>2</sub> must make use of its lobe orbital in order for bonding to occur to both O atoms. Hence the orbital geometry appears to be forcing one of the MO products to be in a particular excited state. Formation of both products in the  $\Sigma^+$  state, or in the  $\Sigma^+$  state and one in the  ${}^{3}\Sigma^{+}$ , would require that the M lobe orbitals move out of alignment with both O atoms. Possibly



Fig. 4. Schematic representation of GVB orbitals of the lowest states of  $M_2$ ,  $O_2$  and MO. Note that the <sup>1.3</sup> $\Pi$  states of MO are formed if a lobe orbital in  $M_2$  is used for bonding to O.

insufficient time or energy is available for this rearrangement to occur. This explanation for the formation of one excited product does not require a symmetric four-centered intermediate, but merely that attachment to the second O atom bypasses surfaces leading to the most stable product states. Yet unexplained is why the  $M+N_2O$  reaction tends to avoid the  $MO(^{3}\Sigma^{+})$  products, which are readily observable in the  $M+NO_2$ .

Future work will involve simulation of spectra to extract product vibrational distributions, which may indicate whether the reactions occur by direct mechanisms. Also, laser-induced fluorescence of ground state products may provide radiative lifetimes needed for determination of absolute cross sections, as well as information on vibrational and rotational distributions.

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