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Stability of Ligand Free Tin–Gold Clusters

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The investigation of metal atom cluster complex compounds has been quite intensive over the last decade.[1] Since recently theoretical interest in ligand free transition metal clusters has been increasing, because such clusters are thought to play a role as active centers in catalysts.[2-4] The only polyatomic intermetallic molecules containing transition metal atoms for which atomization energies have been measured, are triatomic.[5] Here we report the first measured bond energies for intermetallic ligand free transition metal containing molecules with more than 3 atoms. The system tin–gold was chosen for the investigation of such intermetallic clusters, since tin is known to form polyatomic molecules of high stability.[6]

We could identify the intermetallic molecules SnAu, Sn_2Au, $SnAu_2$, Sn_2Au_2 and Sn_3Au and the tin molecules Sn_2 to Sn_6 with a mass spectrometer, over a tin-rich Sn–Au alloy contained in a graphite Knudsen cell. The principles of the method and the experimental procedure have been described elsewhere.[7]

The pressure independent reactions studied, involving tin–gold molecules, are listed in Table 1 together with the corresponding third law enthalpy changes, ΔH°_o, free energy function changes, $-\Delta[(G^\circ_{1600} - H^\circ_o)/T]$ and the number of data sets measured. The temperature range covered was from 1400 to 1900 K. The derived atomization energies, $\Delta H^\circ_{atm,o}(M)$, for the molecules studied, together with the assumed molecular geometries are also given. For SnAu a $^2\pi$ ground state and for the other molecules a $^1\Sigma$ ground state were assumed. The dissociation energy of the tin dimer, $D^\circ_o(Sn_2) = 189.1 \pm 6$kJ mol^{-1}, needed for the calculation of D°_o(SnAu), was also determined. Additional possible geometries chosen for the molecules Sn_3Au and Sn_2Au_2 yielded similar atomization energies.

For all polyatomic intermetallic tin–gold molecules the measured atomization energies are markedly larger than would be expected from the simple bond additivity rule for chain molecules using the values for $D^\circ_o(Sn_2)$ and D°_o(SnAu). This is a strong indication that cluster molecules with their larger number of bonds are preferred over chain formation

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TABLE I. Third-law Reaction Enthalpies and Derived Atomization Energies of Tin–Gold Molecules.

Gas Phase Reaction	No. of Data Sets	$\Delta[(G^\circ_{1600} - H^\circ_o)/T]$ (J K^{-1})	ΔH°_o [a] (kJ)	$\Delta H^\circ_{atm,o}(M)$ [b] (kJ mol^{-1})	Molecule (M)	Assumed Geometry
SnAu + Sn = Sn_2 + Au	19	−11.13	62.3 ± 0.8	251 ± 8	SnAu	
Sn_2Au + Au = 2 SnAu	7	32.51	−16.7 ± 0.8	486 ± 18	Sn_2Au	C_s
$SnAu_2$ + Sn = 2 SnAu	6	40.00	39.3 ± 2.5	542 ± 18	$SnAu_2$	C_{2v}
Sn_2Au_2 + Au = $SnAu_2$ + SnAu	2	74.94	77.0 ± 2.1	871 ± 25	Sn_2Au_2	$D_{\infty h}$
		61.55	54.4	848 ± 25		C_{2v}
Sn_3Au + 2 Au = 3 SnAu	5	90.96	29.7 ± 2.5	786 ± 25	Sn_3Au	$D_{\infty h}$
		80.92	16.3	767 ± 25		C_s

[a] The error terms correspond to standard deviations or deviation from the mean. [b] The error term gives the estimated overall error.

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