Infrared Spectroscopic Evidence for Germanium and Tin Carbonyls

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Summary Co-condensation of germanium or tin atoms with carbon monoxide doped krypton at 20 K leads to the formation of germanium or tin carbonyls; these are detected by i.r. spectroscopy.

Although binary carbonyls of nonmetallic elements, such as H_2CO, F_2CO, OCO, SCO, and $C(CO)_2$ are well known, no binary carbonyls of the sub-Group B metals have so far been found. Recently, the i.r. spectra of $Ni(CO)_4$, $Pd(CO)_4$, and uncharacterized copper and silver carbonyls have been obtained in rare gas matrices[1-3] at 20—27 K by reaction of the metal atoms with CO in the matrix gas. We have conducted similar experiments using the Group IVB elements Ge and Sn, and have obtained i.r. evidence that binary carbonyls of these elements are formed under matrix isolation conditions at 20 K.

The matrix isolation apparatus used has been described elsewhere,[4] and in the present experiments, the metal was evaporated from either alumina or tantalum Knudsen cells, with the furnace temperature adjusted to give metal vapour pressures[5] of *ca.* 10^{-3}—10^{-2} Torr. At these pressures, the vapours of germanium and tin are predominantly monatomic, although small proportions of dimers are also present.[6] The atoms were co-condensed at 20 K with a large excess of Kr containing suitable concentrations of CO. Some of the experiments were repeated with $C^{18}O$.

When Sn vapour was co-deposited with Kr containing $< 0{\cdot}1$ mol % $C^{16}O$, a single strong peak appeared in the i.r. spectrum at 1921 cm^{-1}, in addition to the strong absorption peaks of matrix isolated carbon monoxide,[7] and the weak peaks due to the small amounts of water and carbon dioxide impurities. When the concentration of CO in the matrix gas is increased, the spectra obtained grow increasingly more complex. At 0·5 mol % CO in Kr, additional peaks to the above were obtained at 1864, 1889, 1921, *ca.* 1933, and 1940 cm^{-1}, (see Figure a) and at 1 mol % CO in Kr, further peaks appeared at 1817, 1860, 1901, 1905, and 1944 cm^{-1}, and between 1600 and 1800 cm^{-1}. Some weak peaks were now also observed between 900 and 950 cm^{-1}.

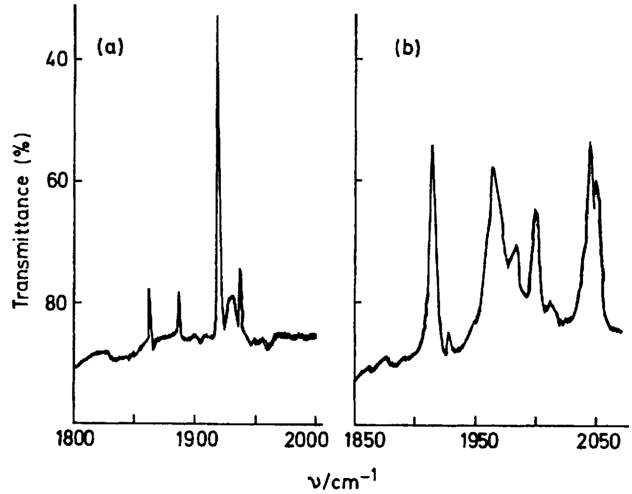

FIGURE. *I.r. spectrum of tin carbonyls at* 20 K. (a) *In* Kr *containing* 0·5 mol % CO, (b) *in* 100% CO.

Repetition of the 0·5% CO experiment using $C^{18}O$ instead of $C^{16}O$ gave a spectrum identical to that obtained with the latter, but with all the peaks shifted to lower frequencies by *ca.* 45 cm^{-1}, an isotopic shift consistent with that expected for a molecule containing carbonyl groups. Tin vapour co-deposited with pure Kr (after extensive degassing of the furnace, to reduce adventitious CO from the hot surfaces) gave no absorption peaks between 1600 and 2100 cm^{-1}. Furthermore, no correlation was observed between the intensities of the H_2O and CO_2 impurity peaks and any of the carbonyl peaks observed, thus ruling out the possibility that the species responsible for the latter peaks contained H_2O or CO_2. We suggest therefore that the compounds formed in the matrix were binary carbonyls of tin.

The frequencies of the peaks observed in the above experiments, together with those observed in matrices containing 10 and 100% CO, are summarized in the Table, and the spectrum obtained from the 100% CO matrix is shown in Figure b.

TABLE

Principal peaks observed in the i.r. carbonyl region for tin atoms in solid carbon monoxide doped Kr.

CO content	<0·1%	½% $C^{16}O$	($C^{18}O$)	1%	10%	100%
Peaks (ν/cm^{-1})[a]				1817		1737
				1830	1825	1825
		1864	(1821)	1864		1840
		1889	(1843)	1888	1892	
				1901		
				1905		
	1921	1921	(1875)	1921	1920	1915
		~1933	(~1887)	~1933	1923	1928
		1940	(1893)	1940		
				1944		
					1952	1966
				1987	1987	1985
					2027	2000
					2045	2046
						2052

[a] Frequency accuracy ± 1 cm^{-1}.

In an experiment with Ge vapour, co-deposited with Kr containing 1 mol % CO, three peaks were seen at 1873, 1878, and 1908 cm^{-1}, while in a similar experiment using pure Kr, a blank spectrum was obtained, suggesting that germanium is also able to form carbonyl species.

Under conditions of low CO concentration in the matrix, we expect that metal rich species will form. We suggest that the 1908 and 1921 cm^{-1} peaks, very prominent under these conditions, are due to the species GeCO and SnCO respectively, analogous to CCO, which is known.[8] The large number of other species apparently possible for tin is illustrated by comparison of Figures a and b, in that none of the peaks that appear in the former are seen in the latter.

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