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Matrix Isolation Electron Paramagnetic Resonance Studies of Tin(II) Fluoride. Evidence for a Vapor Phase Radical Species

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Several recent studies have been published concerning tin in the divalent state. This particular species is interesting from a number of standpoints, including its coordination chemistry [1], structural chemistry [2], and its role in catalyzed processes such as the homogeneous hydrogenation of ethylene [3]. While most of these investigations have been in the solid or solution state, several of them have been in the gas phase. Meier and co-workers, for example, studied the gas phase reaction between tin(II) fluoride and ethylene, with the products being trapped in an argon matrix for spectroscopic study [4]. Other workers [5], using negative ions such as SnX_2^- produced by dissociative resonance capture from parent SnX_4 molecules, determined the electron affinities of $SnCl_2$, $SnBr_2$, and SnI_2. Matrix isolation Mossbauer studies have also been conducted on simple molecules such as SnO [6–8].

In this note, the authors wish to report the argon matrix isolated electron paramagnetic resonance spectrum of tin(II) fluoride, the first evidence for the existence of a radical species in the vapor phase of a divalent tin halide. This research is part of a continuing program in this laboratory involving the chemistry of divalent Main Group IV elements such as silicon [9–11] and tin [4, 5].

Experimental

The matrix isolation electron paramagnetic resonance apparatus has been described previously [11]. Tin(II) fluoride was vaporized from a tantalum foil furnace at 428 °C and co-condensed with argon onto a sapphire rod cold probe. The furnace temperature was measured using a standard chromelalumel thermocouple junction. All spectra were recorded using a Varian Fieldial Mark II electron paramagnetic resonance spectrometer. Trapping times were typically 0.5 h.

Tin(II) fluoride was obtained from two commercial sources (Alfa Ventron and ROC/RIC) so as to minimize the possibility of contaminants contributing to the spectra. Impurities were also monitored by running blank spectra several times during the course of the study.

Discussion

The electron paramagnetic resonance spectra in the present study were calibrated using the methyl radical quartet (this species was conveniently introduced into the system as a pumping oil hydrocarbon contaminant which was pyrolyzed on passing through the furnace and subsequently trapped in the argon matrix), assuming the magnetic field to be linear in this region [11]. The linearity was checked by following the variation of the line position of the methyl radical (as well as the lithium radical [12]) with respect to varying the magnetic field; this technique verified the linearity of the applied field in this region. The spectra of the unknown species were analyzed relative to the methyl radical using a g value of 2.0023 and a hyperfine splitting constant of 64.64 MHz (or 23.1 Gauss) for methyl radicals. The values were previously reported for the methyl radical trapped in an argon matrix [13].

When tin(II) fluoride was vaporized at 428 °C and then co-condensed with argon on the cold-tip probe in the electron paramagnetic resonance spectrometer cavity and the spectrum taken, the results were those shown in Fig. 1. Two sets of slightly overlapping triplets appeared between the two inner lines of the methyl radical quartet used for calibration. A blank background spectrum in this region gave only a baseline, and the use of the two sources of reagent grade SnF_2 limited the possibility of contaminants being responsible for the spectrum. Using the methyl radical line quartet as the internal calibrant, the following g and A values were obtained for the unknown species: $g_{\parallel} = 2.0017$, $g_{\perp} = 2.0013$, $A_{\parallel} = 4.29$ G, and $A_{\perp} = 4.32$ G. The two different splittings are presumably due to anisotropy effects.

The triplets shown in Fig. 1 could arise from a number of species in which an electron is equally coupled with two nuclei of $I = 1/2$. While one possibility might be a tin dimer (formed by dispropor-

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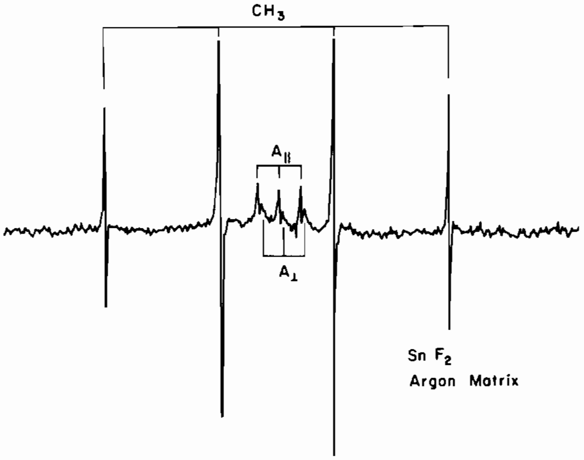

Fig. 1. The electron paramagnetic resonance spectrum of SnF_2 in an argon matrix. The spectrum represents a 100 Gauss scan, and the frequency is 9.702×10^9 s^{-1}. The vaporization temperature was 428 °C, and the trapping time was 0.5 h.

tionation of tin(II) with subsequent combination of the tin atoms), this can be ruled out on the basis of the isotopic abundances and magnetic moments of tin nuclei that have a $I = 1/2$ value. If these isotopes at their abundances were detectable, the spectrum would be considerably more complex than the one obtained*. Even though phosphorescence resulting from a direct transition from the first excited triplet to the ground singlet state has been observed for matrix isolated SnO [14], the existence of triplet SnF_2 here can be precluded due to the relatively low temperature of vaporization used here. Also, there exists a surprising lack of g and A anisotropy that would be expected for a heavy metal fluoride like SnF_2 in a triplet state.

A more logical explanation of the triplets is the coupling of an electron with two ^{19}F nuclei ($I = 1/2$, 100% natural abundance). This would be analogous to the previously reported EPR spectrum of the paramagnetic SiF_2 species generated from lithium and silicon tetrafluoride [11]. The triplet spectrum reported here might logically be assigned to two separate species. First, a simple SnF_2 radical (or diradical) with electron localization on the two fluorine nuclei would give a triplet, with the intensity ratio expected to be 1:2:1. The possibility of a radical dimer is supported by mass spectrometric studies which showed tin(II) fluoride vapor to contain 20% dimer when the vapor was in equilibrium with the solid [15, 16]. Dimerized tin(II) fluoride has also been reported [17] on the basis of matrix isolation infrared studies. An alternate assignment might be an SnF_2^- anion such as in $Sn^+SnF_2^-$. The production of tin clusters has been reported previously [4], and tin metal atoms could serve as a potential perturbing agent when complexed with SnF_2 or $(SnF_2)_2$. A tentative assignment of a complex involving a matrix trapped dimer of SnF_2 and a metal atom has already been published [17]. The hyperfine splitting observed here for the triplet lines in the tin(II) fluoride spectrum is very small, but the value is quite similar to the small splitting in the spectrum of the previously reported silicon(II) fluoride radical [11]; the hyperfine components could alternately result from matrix site splitting or multiple trapping site effects.

The observed triplet intensity pattern shown in Fig. 1 does not appear to be a 1:2:1 triplet that would be expected of a difluoride complex but rather lile a 1:1:1 pattern. At low temperatures, however, the line intensities may vary somewhat; also, the signal to noise ratio of the spectrum is not very high, leading to a complex spectrum that is not well resolved. The possibility of overlapping lines of several species would also preclude an exact 1:2:1 ratio if the other species did not exhibit a 1:2:1 pattern. Unfortunately, attempts at obtaining higher resolution spectra were unsuccessful.

One seemingly obvious experiment would be to study the electron paramagnetic resonance spectra of co-condensed tin metal and tin(II) fluoride or just the condensation of tin metal itself in an argon matrix. Unfortunately, again, because of the tremendous difference in vaporization temperatures (~ 1000 °C for the former and ~ 400 °C for the latter under high vacuum conditions [4]), reproducing the concentration of the two reactants in the matrix in this study would be impossible at the relatively low temperature used here for the vaporization of tin(II) fluoride; also, the vaporization of tin metal at the much higher temperature might introduce radicals that would not be truly typical of those formed at the lower tin(II) fluoride vaporization temperature. One would also again be confronted with the low natural abundance on tin nuclei amenable for use in EPR studies, thus making definitive interpretation again difficult.

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*The difficulty in seeing low abundant nuclei such as ^{119}Sn, ^{13}C, and ^{29}Si in matrix isolated electron paramagnetic resonance spectra has been mentioned previously. Please see ref. 11.

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