Mössbauer Emission Spectra of ^{119m}Sn in Tin Organosol

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(Received July 26, 1984)

Synopsis. The electron-scavenging effects of adding various solutes to a suspension of tin in ethanol were studied by Mössbauer emission spectroscopy. The yield of the aliovalent species of Sn^{4+} as the after-effects of the converted isomeric transition in ^{119m}Sn varied from the value of the suspension of tin in ethanol, depending on the properties of electron trapping of the solute added.

After-effects of converted isomeric transition (CIT) in ^{119m}Sn have been studied by means of Mössbauer spectroscopy.[1–3] As the after-effects, the aliovalent species of oxidized Sn^{4+} were observed in the emission spectra of ^{119m}Sn in the $SnCl_2$ adducts and rapidly frozen solutions of $SnCl_2$, and the species of reduced Sn^{2+} in the $SnBr_4$ adducts.[4–6] The mechanisms of the competing acceptors for the electrons between hot atoms and the surrounding medium for the stabilization of the oxidized Sn^{4+} and autoradiolysis of the ligands for the stabilization of reduced Sn^{2+} were elucidated by taking the properties of the ligands and solvents into consideration.

In this study, an organosol of tin in ethanol containing ^{119m}Sn was prepared and the emission spectra were measured by adding various solutes to the suspension to determine the reactivity of the solute toward the electrons produced in the Auger cascade following CIT in ^{119m}Sn.

Experimental

The sources of the tin organosol were prepared from ^{119m}Sn metal obtained from New England Nuclear Co., according to the method reported previously.[7] For each source, 0.25 mCi of ^{119m}Sn with the specific activity of 0.082 mCi mg^{-1} was suspended in 5 ml of ethanol. The concentration of the solutes added to the suspension in ethanol was 1 mol dm^{-3} except for CH_3I, the concentration of which was 3 mol dm^{-3}.

The emission spectra were measured against the ^{119}Sn enriched $CaSnO_3$ absorber (2.0 mg ^{119}Sn cm^{-2}) at room temperature by cooling the source in a liquid nitrogen cryostat. Mössbauer parameters were deduced from Lorentzian curves computer-fitted to the spectra by the least-squares method.

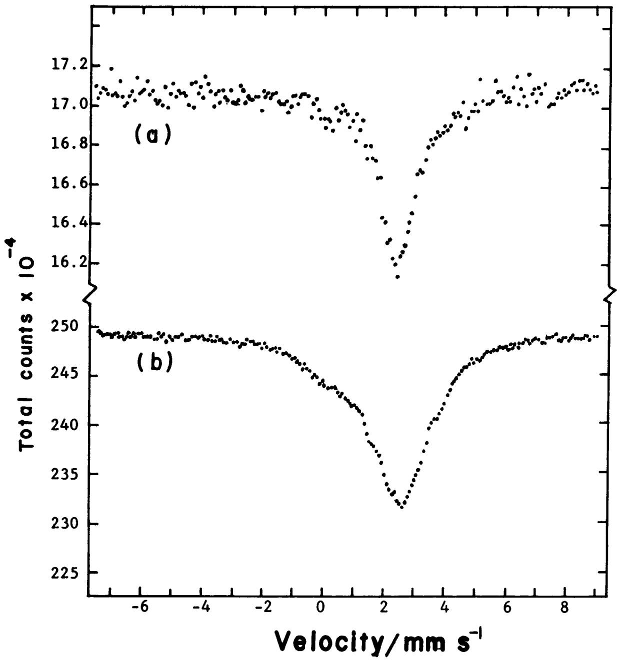

Fig. 1. Mössbauer absorption (a) and emission (b) spectra of the suspension of tin in ethanol at 93 K.

Results and Discussion

The concentration of tin in the suspension was 0.6 mg cm^{-3}, so that the particle size would be about 300 Å and/or less as reported previously.[7] The Mössbauer emission and absorption spectra of the organosol of tin in ethanol are shown in Fig. 1. The absorption spectrum of the organosol of tin in Fig. 1(a) showed that the tin in the suspension was purely β-Sn, but a portion of the oxidized aliovalent species of Sn^{4+} was observed at about 0 mm s^{-1} in the emission spectrum. The emission spectra on adding various solutes to

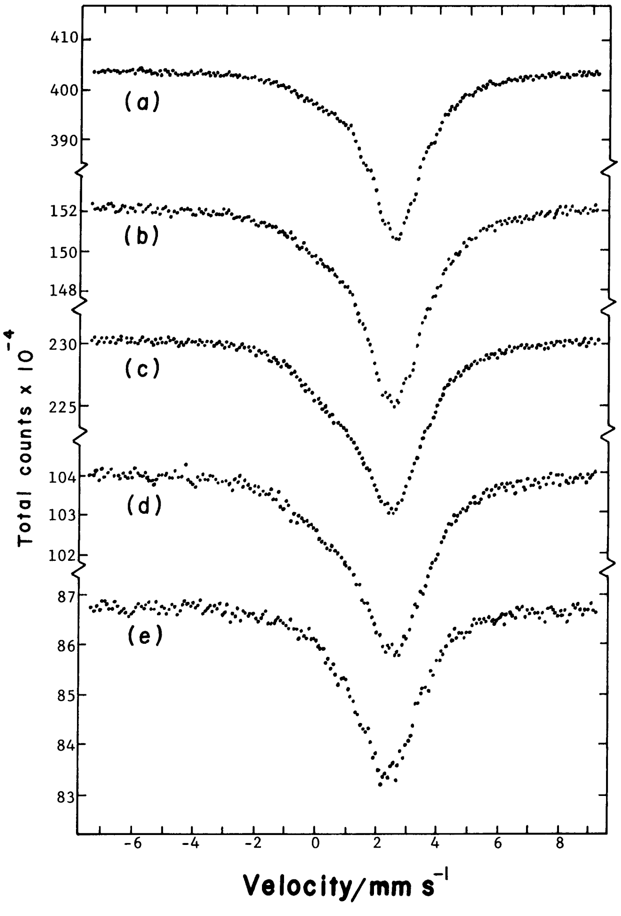

Fig. 2. Mössbauer emission spectra of adding solutes to the suspension of tin in ethanol: (a) $(CH_3)_2SO$; (b) $(C_6H_5)_2SO$; (c) C_5H_5N; (d) CCl_4; (e) CH_3I.

Table 1. Mössbauer emission parameters and area ratio of Sn^{4+} to total for the organosols of tin in ethanol solutions at 93 K

	Sn		Sn^{4+}		$\frac{A(Sn^{4+})}{A(Total)}$ /%
Solute	δ	Γ	δ	Γ	
	$mm\,s^{-1}$	$mm\,s^{-1}$	$mm\,s^{-1}$	$mm\,s^{-1}$	
—	2.58	2.34[a)]	0.17[b)]	2.34[a)]	12.32
$(CH_3)_2SO$	2.58	2.05	0.17	2.05	9.03
$(C_6H_5)_2SO$	2.58	2.35	0.17	2.35	9.62
C_5H_5N	2.56	2.58	0.17	2.58	14.76
CCl_4	2.49	2.46	0.17	2.46	16.81
CH_3I	2.41	2.39	0.17	2.39	5.22

a) Equal line-width. b) Constraining to the value of the suspension in ethanol.

the suspension are shown in Fig. 2. The Mössbauer parameters deduced by constraining the line-width to be equal in both lines of β-Sn and Sn^{4+} and the isomer shift of Sn^{4+} to be 0.17 $mm\,s^{-1}$ of the value of the suspension in ethanol are shown in Table 1 along with the area ratio of Sn^{4+} to the total. The suspension of tin is similar to the solution of $SnCl_2$ in that the electrons emitted by an Auger cascade enter the medium and are trapped by it, stabilizing the aliovalent species of Sn^{4+} in tin microcrystals. The recapture of electrons from the surroundings to return the atom to a normal valence state may be impeded by an insulator formed on the surface of the particle in consequence of the radiolytic effects. The yield of Sn^{4+} in the suspension, 12.32%, was naturally lower than the yield of 28% in the solution of $SnCl_2$ in ethanol reported previously.[6)] However, the increased yield of Sn^{4+} is detected in the suspension by adding CCl_4 and C_5H_5N and the decreased yield by adding $(CH_3)_2SO$, $(C_6H_5)_2SO$, and CH_3I compared with the value of the suspension in ethanol, though the differences in the yield of Sn^{4+} among the emission spectra of the solutions of $SnCl_2$ in C_2H_5OH, $(CH_3)_2SO$, and C_5H_5N are not distinguished clearly.[6)]

In glassy ethanol, the trapped excess electrons generated by ionization have been explained in terms of a small polaron model.[8,9)] This model suggests that the generated Auger electrons following the CIT in ^{119m}Sn are assumed to be trapped by OH groups and shallower traps associated with the alkane moiety; thus the oxidized aliovalent Sn^{4+} species are stabillized. The increased yield of Sn^{4+} by adding CCl_4 can be explained in terms of the well known electron scavenging properties of CCl_4 toward the Auger electrons. Pyridine also increases the yield of Sn^{4+} so that it traps Auger electrons and acts as an electron scavenger in the ethanol solution.

The yield of Sn^{4+} decreases considerably on adding CH_3I though it is a good electron scavenger.[10)] It is well known that CH_3I decomposes to methyl radical-halide anion pairs formed by dissociative electron capture.[11)] The methyl radicals thus created would reduce a portion of aliovalent species of Sn^{4+} to the original state. The decreased yield of Sn^{4+} by adding $(CH_3)_2SO$ can also be explained in the same way as for CH_3I, because $(CH_3)_2SO$ also decomposes to methyl radical-methanesulfenate anion pairs by dissociative electron capture.[12)]

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