Mössbauer Spectroscopic Studies on IT(IC) Decay of ^{119m}Sn in $K_6Sn_2(C_2O_4)_7,4H_2O$

By HIROTOSHI SANO* and MITSUKO KANNO

(*Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Tokyo* 112, *Japan*)

Summary The first experimental evidence for the presence of an "anomalous" charge state in the IT(IC) decay of ^{119m}Sn has been found in ^{119m}Sn-labelled $K_6Sn_2(C_2O_4)_7,4H_2O$.

A NUMBER of cobalt compounds labelled with ^{57}Co used as Mössbauer sources have shown the presence of one or more "anomalous" charge states,[1-3] except cobalt(II) oxalate dihydrate[4] and anhydrous cobalt(II) chloride[2,3] and bromide.[3] Such anomalous charge states have not been observed in the IT(IC) decay of ^{119m}Sn in the various tin compounds so far investigated,[5] *e.g.* tin(IV) oxide and iodide, barium stannate(IV), tetraphenyltin(IV), and tin(II) chloride and iodide. The negative result for the tin compounds has been used by Hazony and Herber[5,6] to support the "internal pressure hypothesis", in order to interpret the origin of anomalous charge states found in ^{57}Co compounds.

We have previously pointed out the remarkable reducing effect of oxalate ion in (n,γ) hot-atom chemistry,[7] radiolysis,[8,9] and photolysis[9] of a number of cobalt and iron compounds. We describe here the Mössbauer spectra of the first excited nuclear state of ^{119}Sn produced in a $K_6Sn_2(C_2O_4)_7,4H_2O$ host crystal labelled with ^{119m}Sn.

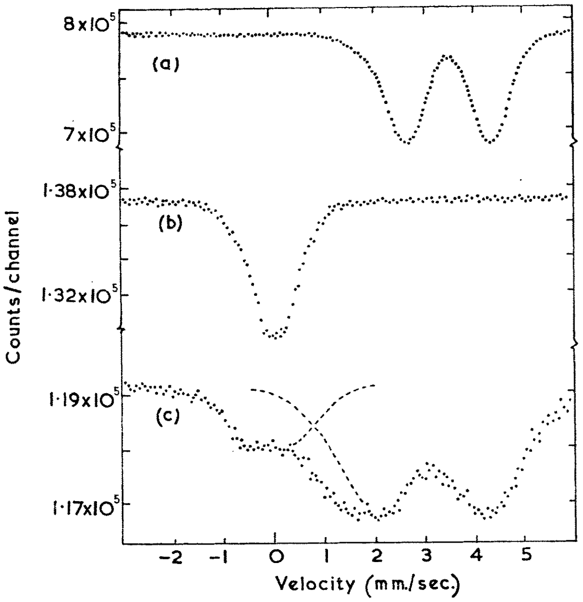

FIGURE. *Mössbauer spectra of (a)* SnC_2O_4 *absorber and* $Ba^{119m}SnO_3$ *source both at* 295° K, *(b)* ^{119m}Sn-*labelled* $K_6Sn_2(C_2O_4)_7,4H_2O$ *"absorber" and* $Ba^{119m}SnO_3$ *source both at* 295° K, *and (c)* $BaSnO_3$ *absorber (kept at* 295° K *and* ^{119m}Sn-*labelled* $K_6Sn_2(C_2O_4)_7,4H_2O$ *"source" (kept at* 79° K).

Colourless crystals of $K_6Sn_2(C_2O_4)_7,4H_2O$ were prepared from metallic tin (isotopic composition: ^{116}Sn 0·92, ^{117}Sn 1·63, ^{118}Sn 91·5, ^{119}Sn 2·14, ^{120}Sn 3·81%; ^{119m}Sn *ca.* 0·1 mc) by the method of Willard and Toribara.[10] The $K_6Sn_2(C_2O_4)_7,4H_2O$ source was kept in a cryostat, and Mössbauer spectra were measured against a barium stannate absorber moving in a constant acceleration mode at room temperature. The $K_6Sn_2(C_2O_4)_7,4H_2O$ labelled with ^{119m}Sn was also used as an "absorber" against a barium stannate source (containing *ca.* 1 mc ^{119m}Sn), in order to confirm the absence of species other than tin(IV). The spectra of tin(II) oxalate and non-radioactive $K_6Sn_2(C_2O_4)_7,4H_2O$ were measured against the barium stannate source for comparison.

Typical spectra are shown in the Figure. The experiment involving barium stannate source and ^{119m}Sn-labelled $K_6Sn_2(C_2O_4)_7,4H_2O$ "absorber" shows the absence of tin(II) species in the host material (see the Figure, b). The experiment using $K_6Sn_2(C_2O_4)_7,4H_2O$ "source" and barium stannate absorber, both at room temperature, shows no resonance; whereas in the case of barium stannate source and $K_6Sn_2(C_2O_4)_7,4H_2O$ absorber (either ^{119m}Sn-labelled or unlabelled) a quite high resonance intensity is evident even at room temperature. The resonance intensity in the case of the $K_6Sn_2(C_2O_4)_7,4H_2O$ source (kept at 79° K) and barium stannate absorber (295° K) was much lower than that for the barium stannate source (295° K) and $K_6Sn_2(C_2O_4)_7,4H_2O$ absorber (79° K). From the results, it may be concluded that; (1) the IT(IC) decay of ^{119m}Sn in $K_6Sn_2(C_2O_4)_7,4H_2O$ gives rise principally to tin(II); and (2) the recoil-free fraction of the ^{119}Sn produced through the decay process is smaller than that of the host tin(IV) atoms, indicating that some lattice damages are produced around the decayed atoms.

This first experimental evidence for the chemical effect—the presence of an "anomalous" charge state—in the IT(IC) decay of ^{119m}Sn may be ascribed to the electronic excitation–de-excitation process (similar to the radiation or photochemical process) of the oxalate ligands initiated by the ^{119}Sn IC-Auger effect. The latter would be followed by the decomposition of the oxalate ions to carbon dioxide and the reduction of $^{119}Sn^{IV}$ to $^{119}Sn^{II}$ species. The minor component in the spectrum (Figure, c) indicates some retention of the decayed ^{119}Sn atoms in the tin(IV) state, whereas $^{57}Fe^{III}$ has never been detected in the EC decay of ^{57}Co oxalate compounds, such as cobalt(II) oxalate[3] and potassium trisoxalatocobaltate(III).[11] This may be attributed, in part at least, to the higher fluorescence yield in tin as opposed to iron.

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[1] G. K. Wertheim, *Phys. Rev.*, 1961, **124**, 764; G. K. Wertheim, W. R. Kingston, and R. H. Herber, *J. Chem. Phys.*, 1962, **37**, 687; G. K. Wertheim and R. H. Herber, *ibid.*, 1963, **38**, 2106; G. K. Wertheim and H. J. Guggenheim, *ibid.*, 1965, **42**, 3873; R. Ingalls and G. DePasquali, *Phys. Letters*, 1965, **15**, 262; W. Trifthäuser and P. Craig, *Phys. Rev. Letters*, 1966, **16**, 1161; J. M. Friedt and J. P. Adloff, *Compt. rend.*, 1967, **264**, *B*, 1356.

[2] J. G. Mullen, *Phys. Rev.*, 1963, **131**, 1410.

[3] H. Sano, M. Aratani, M. Kanno, and K. Sato, *Radioisotopes*, to be published.

[4] H. Sano and F. Hashimoto, *Bull. Chem. Soc. Japan*, 1965, **38**, 1565.

[5] See comments by R. H. Herber, *Proceedings of the Symposia of the Faraday Society, No.* 1. *The Mössbauer Effect*, 1967, pp. 19 and 101.

[6] Y. Hazony and R. H. Herber, *J. Inorg. Nuclear Chem.*, 1969, **31**, 321.

[7] N. Saito, H. Sano, and T. Tominaga, *Chem. and Ind.*, 1964, 1622.

[8] H. Sano, N. Matsubara, and N. Saito, *Bull. Chem. Soc. Japan*, 1965, **38**, 333.

[9] N. Saito, H. Sano, T. Tominaga, and F. Ambe, *Bull. Chem. Soc. Japan*, 1965, **38**, 681.

[10] H. H. Willard and T. Y. Toribara, *J. Amer. Chem. Soc.*, 1942, **64**, 1759.

[11] J. P. Adloff, personal communication.