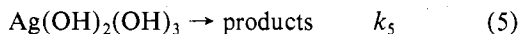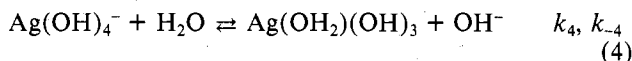by a two-electron path,[4,5,7,8,10] (b) Ag^+ is the final product and does not absorb at 267 nm, and (c) Ag(II) would either react very slowly by a first-order path[7] or undergo disproportionation which would result in an Ag^+ dependence (cf. Table II). In addition, although Ag(II) is probably deprotonated at these low acidities,[16,17] very rapid reduction of $Ag(OH)_4^-$ to $AgOH^+$ in the initial step would require a rate constant for $AgOH^+$ reduction which is 6 orders of magnitude larger than that reported in ref 7 for the first-order reduction of Ag(II).

(4) Using the equilibrium constant for Ag(II) disproportionation given by Po et al.[7] along with their kinetic data, we estimate a first-order rate constant of about 1 s^{-1} for the reaction of AgO^+ with water. This seems to rule out AgO^+ as the reactant under our conditions since ionic strength differences and the effect of nitrate complexation[16] and hydrolysis of Ag(II) would be insufficient to explain an increase of more than 2 orders of magnitude.

At the low Ag(III) concentrations and short time scale of this study, precipitation of solid $Ag(OH)_3$ does not seem important. However, a small degree of polymerization might be an additional source of the observed experimental deviations.

Since reaction 2 is complete in less than 2 ms, even at 0.0025 M H^+, we are able to estimate that $k_2 > 5.5 \times 10^5$ M^{-1} s^{-1}. We would, in fact, expect this reaction to be even faster with k_2 close to the diffusion-controlled limit.

Spectral measurements and the relative stability of Ag(III) indicate that $Ag(OH)_4^-$ is the only important Ag(III) species in base down to at least 0.1 M OH^-.[1,2] When an $Ag(OH)_4^-$ solution is rapidly brought to pH 11, decomposition occurs within 1 or 2 s at 30 °C.[3] This latter observation is consistent with a mechanism in which formation of $Ag(OH_2)(OH)_3$ is rate determining (eq 4 and 5).

$$Ag(OH)_4^- + H_2O \rightleftharpoons Ag(OH_2)(OH)_3 + OH^- \qquad k_4, k_{-4}$$
$$(4)$$

$$Ag(OH)_2(OH)_3 \rightarrow \text{products} \qquad k_5 \qquad (5)$$

Since solid silver oxides are formed under these conditions, k_5 would probably be somewhere between k_2 and $2k_2$ depending on how effectively the conproportionation reaction between Ag(III) and Ag(I) competes with the reduction of Ag(III). The rate constant k_4 has, in fact, been determined from the solvent path for ethylenediamine substitution of Ag(III),[18] and its value of 0.6 s^{-1} is in good qualitative agreement with the decomposition rate at pH 11. Furthermore, the fact that the reverse of reaction 4 suppresses rapid decomposition at 0.1 M OH^- but not at $[OH^-] \approx 10^{-3}$ M leads to a rough estimate of $K_4 \approx 10^{-3}$ M.

Registry No. $Ag(OH)_4^-$, 23172-26-1.

References and Notes

(1) G. L. Cohen and G. Atkinson, *J. Electrochem. Soc.*, **115**, 1236 (1968).
(2) L. J. Kirschenbaum, J. H. Ambrus, and G. Atkinson, *Inorg. Chem.*, **12**, 2832 (1973).
(3) L. J. Kirschenbaum and G. Atkinson, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, IL., 1970, No. INOR 57.
(4) (a) A. A. Noyes, J. L. Hoard, and K. S. Pitzer, *J. Am. Chem. Soc.*, **57**, 1221 (1935); (b) A. A. Noyes, C. D. Coryell, F. Stitt, and A. Kossiakoff, *ibid.*, **59**, 1316 (1937).
(5) J. B. Kirwin, F. D. Peat, P. J. Proll, and L. H. Sutcliff, *J. Phys. Chem.*, **67**, 1617 (1963).
(6) G. A. Rechnitz and S. B. Zamochnick, *Talanta*, **11**, 713, 1645 (1964); **12**, 479 (1965).
(7) H. N. Po, J. H. Swinehart, and T. L. Allen, *Inorg. Chem.*, **7**, 244 (1968).
(8) B. M. Gordon and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 273 (1958).
(9) D. H. Huchital, N. Sutin, and B. Warnquist, *Inorg. Chem.*, **6**, 838 (1967).
(10) A. Viste, D. A. Holm, P. L. Wang, and G. D. Veith, *Inorg. Chem.*, **10**, 631 (1971).
(11) A. A. Noyes, K. S. Pitzer, and C. L. Dunn, *J. Am. Chem. Soc.*, **57**, 1229 (1935).
(12) W. M. Latimer, "Oxidation Potentials", 2nd ed., Prentice-Hall, Englewood Cliffs, N.J., 1952, p 189.
(13) (a) Reference 12, p 192; (b) H. L. Johnston and H. L. Leland, *J. Am. Chem. Soc.*, **60**, 1439 (1938).
(14) W. Feitknecht and P. Schindler, *Pure Appl. Chem.*, **6**, 139 (1963).
(15) H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964).
(16) D. S. Honig and K. Kustin, *J. Inorg. Nucl. Chem.*, **32**, 1599 (1970).
(17) D. S. Honig, K. Kustin, and J. F. Martin, *Inorg. Chem.*, **11**, 1895 (1972).
(18) L. J. Kirschenbaum, *J. Inorg. Nucl. Chem.*, **38**, 881 (1976).

Contribution from the Nuclear Research Center
"Demokritos", Athens, Greece

¹¹⁹Sn Mössbauer Spectroscopy of Polynuclear Dithiooxalate Copper(I)–Tin(IV) Complexes

D. Petridis

The dithiooxalate ligand, $(C_2S_2O_2)^{2-}$, dto, has the important property of acting as a multifunctional complexing agent.[1-4] The dianionic ligand may be O,O, S,S, or O,S bonded to a variety of metal ions according to the particular preference of the metal for "hard" or "soft" ligands. In addition, under appropriate conditions, the ligand may coordinate to more than one metal ion forming polynuclear complexes. A series of such complexes containing Sn(IV) and Cu(I) centers has been recently described by Coucouvanis and Leitheiser.[5] The complexes are of the general type $M[(O_2C_2S_2)Cu(PPh_3)_2]_n$: $M = Cl_4Sn^{IV}$, $CH_3Cl_3Sn^{IV}$, $(CH_3)_2Cl_2Sn^{IV}$, $n = 1$, I; $M = Cl_2Sn^{IV}$, CH_3ClSn^{IV}, $(CH_3)_2Sn^{IV}$, $n = 2$, II; $M = CH_3Sn^{IV}$, $ClSn^{IV}$, $BrSn^{IV}$, $n = 3$, III.

I , X = Cl , CH₃

II , X = Cl , CH₃

III , X = Cl , Br , CH₃

L = PPh₃
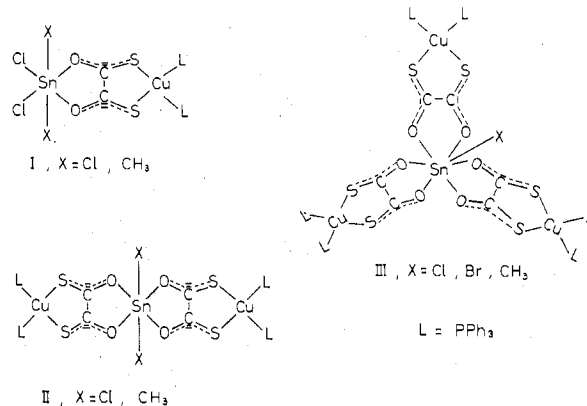
The mode of coordination of the dithiooxalate ligands toward Cu(I) and Sn(IV) and conceivable structures of the complexes were deduced from infrared and NMR spectroscopy. In this note we report on the ¹¹⁹ᵐSn Mössbauer spectra of the above polynuclear complexes; the spectra assist in determining the stereochemistry at the tin site and also in determining the bonding properties of the dithiooxalate ligand toward tin.

Experimental Section

Samples of the complexes were supplied by Professor Coucouvanis. Their preparation and characterization has been reported.[5] Mössbauer spectra were measured on a constant-acceleration spectrometer. Absorbers were maintained at 80 ± 2 K and a source of Ba¹¹⁹SnO₃ was used at room temperature. The spectrometer was calibrated periodically by using the magnetic hyperfine spectrum of an iron-foil absorber. Relative errors were less than ±0.5 mm/s. The parameters were obtained by a least-squares computer fit of the data. In comparing the isomer shifts of different compounds, we assume that the shifts of SnO_2 and $BaSnO_3$ are identical.

Table I. Mössbauer,[a] Infrared, and Electronic Absorption Data of the Complexes

complex	IS	QS	Γ_1	Γ_2	IR, C=O,[b] cm^{-1}	$10^{-3}\lambda_{max}$,[b] cm^{-1}
1 $Cl_2Sn(O_2C_2S_2)Cu(PPh_3)_{2,2}$	0.46		0.52		1352 s	20.8
2 $MeSnCl(O_2C_2S_2)Cu(PPh_3)_{2,2}$	0.71	1.76	0.40	0.37	1365 s	21.7
3 $Me_2Sn(O_2C_2S_2)Cu(PPh_3)_{2,2}$	0.96	2.50	0.42	0.34	1381 s	23.3
4 $(BzPh_3P)Cu(S_2C_2O_2)(PPh_3)_2SnCl_4$	0.52		0.45		1402 s	22.2
5 $(BzPh_3P)Cu(S_2C_2O_2)(PPh_3)_2MeSnCl_3$	0.80	1.90	0.45	0.49	1421 s	23.8
6 $(BzPh_3P)Cu(S_2C_2O_2)(PPh_3)_2Me_2SnCl_2$	1.39	3.87	0.45	0.56	1447 s	25.6
7 $ClSn(O_2C_2S_2)Cu(PPh_3)_{2,3}$	0.15		0.64		1368 s	
8 $BrSn(O_2C_2S_2)Cu(PPh_3)_{2,3}$	0.38		0.54		1364 s	
9 $MeSn(O_2C_2S_2)Cu(PPh_3)_{2,3}$	0.76	1.98	0.36	0.41	1392 s	
10 $K_2Sn(S_2C_2O_2)_3$	0.85		0.58		1600 s, b	
11 $KSn(C_2S_2O_2)_3Cu(PPh_3)_2$	0.50	0.81	0.51	0.60	1627 s, 1371 s	

[a] IS, QS, Γ_1, and Γ_2 are in mm/s; absorber temperature 78 K; IS is expressed relative to $BaSnO_3$ at room temperature; IS and QS are ±0.04 mm/s. [b] Data from ref 5.

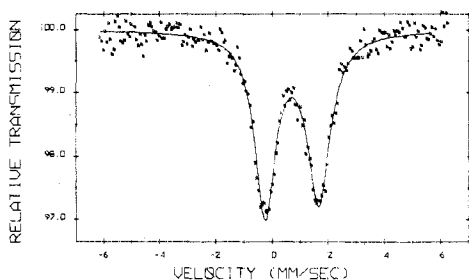**Figure 1.** Mössbauer spectrum of $(BzPh_3P)Cu(S_2C_2O_2)$-$(PPh_3)_2SnMeCl_3$ at 77 K.

Results and Discussion

Pertinent Mössbauer parameters are listed in Table I. A typical spectrum is shown in Figure 1. The infrared spectra of all complexes show strong absorption around 1400 cm^{-1}, which is considered as evidence for coordination of tin to the α-diketone portion of the dto ligand.[5] The Mössbauer results are also in agreement with this mode of coordination. When data for comparison are available, the isomer shifts of the present complexes are closer to the shifts from other known six-coordinate tin(IV) complexes containing O,O chelating ligands than to those of S,S chelating ligands, presumably due to the different electron-releasing power of oxygen and sulfur. The isomer shift of compound **4** for instance, 0.52 mm/s, is almost the same with the reported value of 0.51 mm/s for $SnCl_4(MeO(CH_2)_2OMe)$, but it is quite different from the shift of the analogous S,S chelate $SnCl_4(SMe(CH_2)_2SMe)$,[6] 0.70 mm/s. Similarly, when the spectra are quadrupole split, the observed splittings compare well with the data reported for many model $RXSn(OO)_2$ or $R_2Sn(OO)_2$ compounds.[7]

Compound **1** of the $Cl_2Sn(OO)_2$ type features a one-line spectrum analogous with those of other complexes having O,O ligands.[8] In contrast, the spectrum of $Cl_2Sn(2-S(py)O)_2$, a compound containing the S,O-chelated anion of 2-pyridethiol 1-oxide, has been reported to have a small quadrupole splitting.[9] We have reconfirmed the two lines by measuring the spectrum in our spectrometer. The different spectra appear to oppose the possibility of S,O coordination of the dto ligands in **1**. Compound **11** shows a similarly small but discrete quadrupole splitting. An X-ray study[10] of this compound has shown that one of the dithiooxalates is O,O chelated to tin and the other two are S,S chelated to tin. On the other hand, compound **10** with only S,S-bonded dithiooxalate groups exhibits an unsplit spectrum in agreement with other $Sn(SS)_3$ compounds.[11] It seems that in Sn(SO) chelation the imbalance in the polarities of tin–ligand σ bonds is sufficient to produce an electric-field gradient at the tin nucleus, while it is not in O,O or S,S chelation.

The isomer shifts in complexes **1–3**, **4–6**, and **7–9** vary in a systematic way with the electron-withdrawing ability of the
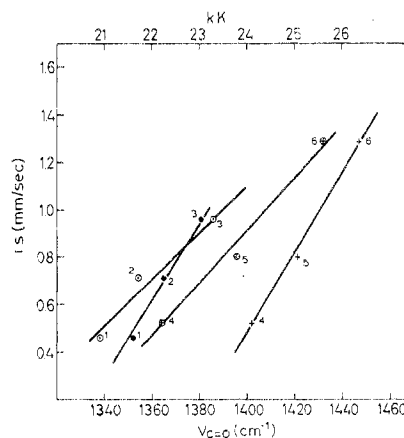

Figure 2. Correlation between the isomer shift, the C=O stretching frequency (cm^{-1}), and the Cu→S charge-transfer band (×10^3 cm^{-1}) in polynuclear dithiooxalato complexes of tin. The numbering scheme is the same as the one used in Table I. ● and + refer to plots of IS vs. the position of the C=O absorption; ⊙ and ⊕ refer to plots of IS vs. the Cu→S charge transfer.

ligands. In a simple manner, increasing polarity of the tin-to-ligand bonds results in lower shifts because of the diminution in s-electron density at the tin nucleus. This effect is especially pronounced in the progressive replacement of chlorine atoms by methyl groups. On the other hand, the electron-withdrawing abilities of the substituents on tin are also expected to affect the C=O stretching vibration of the coordinated dithiooxalate ligand. A substituent of high electron-withdrawing power will increase the Lewis acidity of the stannic compound resulting in a strenthening of the C=O→Sn dative bonds and consequently in a weaking of the C=O stretching vibration. In addition, it was found that the inductive effects of the various substituents on tin cause a bathochromic shift in the absorption band associated with a Cu → S charge transfer.[5] In view of these effects, the isomer shift is expected to vary linearly with the C=O stretching frequency or the position of the Cu → S charge-transfer band. Such correlations were indeed observed for the homologous series **1–3** and **4–6** and are shown in Figure 2.

The Mössbauer parameters for compounds **7** and **9** are similar to those of $SnCl(trop)_3$, IS = 0.12 mm/s, and $MeSn(trop)_3$, IS = 0.76 mm/s, QS = 1.98 mm/s.[8] Since the tropolinates are known seven-coordinate complexes of tin,[12] the similarities in the Mössbauer spectra indicate the same coordination number for tin in the polynuclear complexes.

The large quadrupole splitting obtained for **6** indicates a trans Me–Sn–Me configuration in agreement with other similar trans complexes; e.g., the QS of *trans*-$Me_2SnCl_2(pyO)_2$, the structure of which is known from X-ray analysis,[13] is 3.96 mm/s.[14] On the other hand, the QS of **3**, 2.50 mm/s, is

appreciably lower than 3.95 mm/s for *trans*-Me₂Sn(acac)₂.[15] Since for R₂SnL₄ complexes the ratio QS(trans):QS(cis) is 2:1, it is likely that in **3** an approximate cis arrangement occurs.

$$\begin{array}{c} \text{Me} \\ \backslash \\ \text{Sn} \\ / \\ \text{Me} \end{array}$$

Acknowledgment. The author thanks Professor Coucouvanis for providing the samples and for making available his result on the dithiooxalate copper(I)–tin(IV) complexes prior to publication.

Registry No. 1, 62392-92-1; **2**, 62392-91-0; **3**, 62392-90-9; **4**, 62476-50-0; **5**, 62476-49-7; **6**, 62476-48-6; **7**, 62430-63-1; **8**, 62430-62-0; **9**, 62430-64-2; **10**, 62415-55-8; **11**, 62430-60-8.

References and Notes

(1) D. Coucouvanis, N. C. Baenziger, and S. M. Johnson, *J. Am. Chem. Soc.*, **95**, 3875 (1973).
(2) D. H. Piltingsrud and D. Coucouvanis, *J. Am. Chem. Soc.*, **95**, 5556 (1973).
(3) D. Coucouvanis, *J. Am. Chem. Soc.*, **93**, 1786 (1971).
(4) F. J. Hollander and D. Coucouvanis, *Inorg. Chem.*, **13**, 2381 (1974).
(5) M. L. Leitheiser and D. Coucouvanis, *Inorg. Chem.*, **16**, 1611 (1977).
(6) J. Philip, M. A. Mullins, and C. Curran, *Inorg. Chem.*, **7**, 1895 (1968).
(7) (a) R. V. Parish, *Prog. Inorg. Chem.*, **15**, (1972); (b) G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, **15**, (1972).
(8) D. V. Naik, J. C. May, and C. Curran, *J. Coord. Chem.*, **2**, 309 (1973).
(9) D. Petridis, F. P. Mullins, and C. Curran, *Inorg. Chem.*, **9**, 1270 (1970).
(10) F. J. Hollander, M. Leitheiser, and D. Coucouvanis, *Inorg. Chem.*, **16**, 1615 (1977).
(11) D. Petridis and B. W. Fitzsimmons, *Inorg. Chim. Acta*, **11**, 105 (1974).
(12) J. J. Park, D. M. Collins, and J. L. Hoard, *J. Am. Chem. Soc.*, **92**, 3636 (1970).
(13) E. A. Blum, B. R. Penfold, and W. T. Robinson, *J. Chem. Soc. A*, 913 (1969).
(14) A. G. Davies, L. Smith, and P. J. Smith, *J. Organomet. Chem.*, **23**, 135 (1970).
(15) (a) B. W. Fitzsimmons, N. J. Seeley, and A. W. Smith, *Chem. Commun.*, **7**, 390 (1968); (b) R. H. Herber and M. F. Leahy, *J. Chem. Phys.*, **60**, 5070 (1974).


Mechanism for the Isothermal Decomposition of Iron Titanium Hydride

D. L. Lindner

The stoichiometric alloy FeTi has been the center of a great deal of interest as a result of its ability to absorb and desorb hydrogen under conditions which are suited to storage of the gas for use as a source of energy. Reilly and Wiswall[1] were the first to investigate the properties of hydrides of the alloy. While their primary concern was the investigation of the phase diagram of the Fe–Ti–H system, they also conducted studies of both its hydriding and its dehydriding kinetics.[2]

They found that the kinetics of the isothermal decomposition reaction appeared to be first order for most of the reaction. They also noted an apparent divergence from these kinetics at short times. It was speculated that this divergence was a result of differences in behavior between the higher and lower hydrides of FeTi.

Historically, there has been a good deal of research into the kinetics of decomposition reactions[3,4] of the type

$$A(\text{solid}) \rightarrow B(\text{solid}) + C(\text{gas})$$
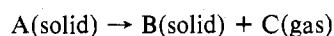
which includes the dehydriding reaction being considered here. In general, it has been observed that such reactions are quite
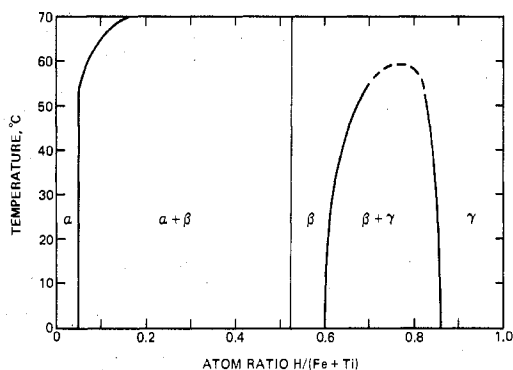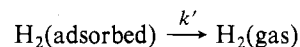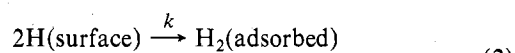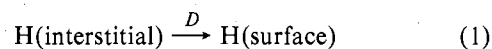

Figure 1. Phase diagram for the Fe–Ti–H system; after Reilly and Wiswall.[1]

complicated. Usually such phenomena as nucleation of the product lattice, growth of such nuclei, and cracking of the reactant lattice due to strain from product lattice growth, as well as a variety of other such topochemical processes, can determine the kinetics of decomposition. To our knowledge, no systems other than metal hydrides exhibit apparent first-order decomposition kinetics.

Decomposition of iron titanium hydride under vacuum by first-order kinetics indicates that at any time each hydrogen atom has a probability of being lost to the vacuum equal to that of any other hydrogen atom. In the usual case during decomposition, the probability that any particular atom of the gas-forming species will be lost is determined by topochemical factors such as proximity to a phase boundary. Consequently, the probability of loss of a particular atom or molecule of the gas-forming species is not a constant but instead varies widely for particular atoms in the solid.

A partially decomposed sample of iron titanium hydride should contain phase boundaries (see Figure 1) and decomposition kinetics could thus be affected by them. The fact that the kinetics are not so affected indicates that some process which averages the environment of each hydrogen atom is active and of prime importance to the decomposition of this hydride. The relatively rapid diffusion of hydrogen in the hydride lattice is one such process and is the basis of the model described below. By contrast, the diffusion of the gas-forming species in other solids which undergo endothermic decompositions (e.g., carbon dioxide in carbonates, or water in hydroxides) is relatively very slow and such environmental averaging does not occur, giving rise to the normal topochemical control of decomposition.

We can postulate that a metal hydride decomposes by the series of reactions in eq 1 and 2, where the diffusion process

$$H(\text{interstitial}) \xrightarrow{D} H(\text{surface}) \tag{1}$$

$$2H(\text{surface}) \xrightarrow{k} H_2(\text{adsorbed})$$
$$H_2(\text{adsorbed}) \xrightarrow{k'} H_2(\text{gas}) \tag{2}$$

in the first step is fast enough to average out the topochemical features which normally dominate the kinetics of decomposition reactions. For a particular metal hydride either step 1 or step 2 could be rate determining (in practice the two reactions of step 2 would be difficult to separate).

Microscopic investigation of iron titanium hydride shows that after a few hydriding–dehydriding cycles the alloy particles are split into block or platelike fragments by an extensive series of fine cracks. Characteristic dimensions of the resulting interlocked fragments are on the order 2–10 μm.[5] It therefore seems reasonable to compare the kinetics of decomposition of this system with those predicted by the equation for diffusion out of a slab.