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A Proton Magnetic Resonance and Electron Diffraction Study of the Thermal Decomposition of Tin(IV) Hydroxides

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Electron diffraction and proton magnetic resonance techniques were used to study the dehydration of tin(IV) hydroxide to cassiterite. Thermogravimetric curves exhibited points of inflection which are attributed to definite crystalline compounds because the corresponding powders produced sharp electron diffraction lines. Formulas based on chemical analysis are proposed for the dehydration stages, as is a possible, over-all dehydration mechanism. The various dehydration stages were studied by observing the temperature dependence from 80 to 300°K of their broad proton magnetic resonance line shapes. Analysis of the line shape for the first dehydration stage SnO_3H_2, at 80°K, indicates that the protons occur in OH groups arranged such that three or more protons are clustered together. The analysis is complicated by some motional narrowing of the absorption line, which persists at 80°K. The temperature range over which the line shape broadens is large, suggesting that more than one type of motion is involved. Motional narrowing does not appear to be present at 80°K in the second dehydration stage, $Sn_2O_5H_2$, but the absorption line is much narrower and indicates that the protons occur in isolated OH groups. The proton magnetic resonance was too weak in the third and fourth dehydration stages to provide useful data.

Introduction

There has been some interest in the past[2,3] in the semiconducting properties of tin(IV) oxide. In this connection, it is not at all clear how to formulate the production of a nonstoichiometric type of semiconductor from tin oxide. Much of the literature available on this topic is found in patents.[4-6]

A laboratory preparation of tin oxide usually starts from water-soluble Sn^{4+}-containing salts, which yield a gelatinous precipitate of the corresponding hydroxide in alkaline or neutral medium. Subsequent washing and drying and eventual heating to about 600° produces a white solid which has the structure of naturally occurring tin(IV) oxide, cassiterite, which has the rutile structure. Apart from the disagreement with regard to the melting point[7] of this material, the dehydration mechanism by which cassiterite is obtained from tin hydroxide is by no means clear. Some authors regard the initial hydroxide as colloidal tin oxide in combination with water, while others regard the intermediate stages as oxyhydroxytin compounds.[8,9] Colloidal tin oxide in combination with water should be amorphous, giving a diffuse X-ray powder pattern, as opposed to well-defined lines being expected for the crystalline oxyhydroxy compounds. X-Ray diffraction of powdered tin hydroxide and subsequent dehydration stages[8,10] did not give a clear answer to the above-mentioned controversy. Instead of well-defined sharp lines, the lines that appeared were of a diffuse nature.

The present study was initiated by P. K. with the hope that it would elucidate the nature of the SnO_2–H_2O system and perhaps help to explain its complex electrochemical behavior. In particular, it was thought that an electron diffraction study of tin hydroxide and of its dehydration products, which has not been published so far, could be useful in deciding whether the dehydration products are amorphous or crystalline. Furthermore, the number of protons and their configuration should change drastically during the dehydration of tin hydroxide. A line-shape study of the proton magnetic resonance absorption yields information about the neighboring magnetic nuclei, their position, and number. The temperature dependence of the line shape yields information about the motions of the protons within the solid. So it should be interesting to study the dehydration of tin hydroxide by proton magnetic resonance, including a temperature dependence study of each dehydration stage.

Experimental Section

Sample Preparation.—Mixing a 2 *M* $SnCl_4$ solution with an equivalent amount of NH_4OH produced the $Sn(OH)_4$ precipitate. It is desirable to mix the reagents rapidly so as to obtain small particles; otherwise the excess Cl^- and NH_4OH are difficult to remove from the precipitate. Purification of the precipitate was achieved by successive washings with redistilled water until the washings gave no positive reaction for NH_4^+ and Cl^- ions. During this washing (30 days) a gel was formed which was then cut up into small pieces. Thereafter the gel was dried by subjecting it to a dry-air stream at room temperature for 15 days followed by heating it to 110° at atmospheric pressure until a constant weight was achieved. The resulting product, though slightly hygroscopic, had nevertheless a reproducible chemical analysis, corresponding to the empirical formula SnO_3H_2. *Anal.* Calcd for SnO_3H_2: Sn, 70.36; H, 1.19. Found: Sn, 69.8; H, 1.2. This sample was used in the thermogravimetric analysis (tga)[11] and products of the latter were subjected to electron diffraction and nuclear magnetic resonance study.

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Electron Diffraction.—For this investigation we used a Siemens Electronmicroscope I having a double condenser with a 5-μa beam and an accelerating potential of 100 kv. The standard was a Au polycrystalline sample. The powder to be investigated was supported on a colloidon membrane.[12]

Nuclear Magnetic Resonance.—The broad-line magnetic resonance spectrometer has been described previously.[13] The magnetic field was modulated at 30 Hz, the amplitude of which depended on the line width. In the temperature-dependence studies, a gas-flow cryostat was used with cold nitrogen to cover the temperature range from room temperature to 120°K. This cryostat was used with a permanent magnet of field strength 4180 gauss. For lower temperatures, down to 80°K, a heat-leak cryostat was used in conjunction with a permanent magnet of field strength 6325 gauss.[13] In both instances the magnetic field was swept linearly in time while the oscillator frequency was kept constant. Numerical integration of the experimentally observed first derivative of the absorption yielded a second moment which was corrected for modulation broadening by means of the expression given by Andrew.[14] All of the data were obtained for samples which were in the form of fine powders.

Results and Discussion

Thermogravimetric Analysis.—The tga of the original sample of SnO_3H_2, at 580 mm, indicates four dehydration steps,[11] as shown in Figure 1. Upon being heated, the white product becomes green-black at 320°, but above 550° it is again white. In order to elucidate the tga curve, samples were removed from the bulk material at various stages, as indicated by vertical arrows in Figure 1, and subjected to conventional combustion analysis using a stream of oxygen. The hydrogen content was determined by the water evolved, tin was determined from the weight of the SnO_2 residue, and oxygen was calculated by difference. According to the findings of the chemical analysis, we suggest that the dehydration occurs *via* the following steps, involving the intermediate formation of partially reduced material (III and IV): at about 250°

$$\underset{\text{I}}{2SnO_3H_2} \longrightarrow \underset{\text{II}}{Sn_2O_5H_2}$$

between 325 and 360°

$$\underset{\text{II}}{2Sn_2O_5H_2} \longrightarrow \underset{\text{III}}{Sn_4O_9H_3}$$

at about 500°

$$\underset{\text{III}}{2Sn_4O_9H_3} \longrightarrow \underset{\text{IV}}{Sn_8O_{16}H_2}$$

above 600°

$$\underset{\text{IV}}{Sn_8O_{16}H_2} \longrightarrow \underset{\text{V}}{SnO_2}$$

A comparison of the experimental and postulated compositions is given in Table I.

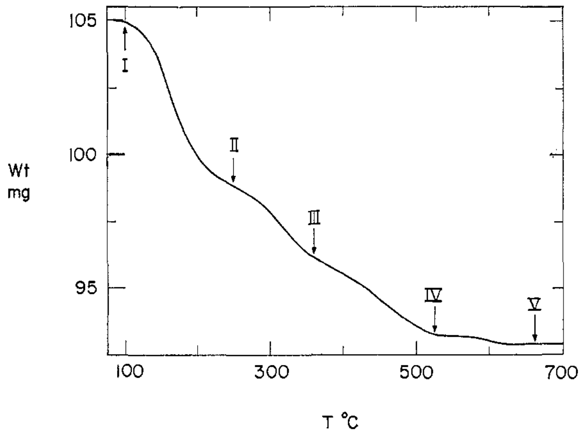

Figure 1.—Thermogravimetric analysis curve of the product SnO_3H_2 (I) obtained by drying $Sn(OH)_4$. The arrows correspond to the compositions given in Table I.

TABLE I

COMPOSITIONS AND PROPOSED FORMULAS OF DEHYDRATION PRODUCTS OBTAINED FROM $Sn(OH)_4$

Substance	Temp range, °C	Compn,[a] % Sn	H
I	100–110	69.8	1.2
SnO_3H_2		70.36	1.19
II	250	73.92	0.67
$Sn_2O_5H_2$		74.30	0.63
III	325–360	76.1	0.51
$Sn_4O_9H_3$		76.35	0.49
IV	500	77.9	0.21
$Sn_8O_{16}H_2$		78.63	0.17
V	Above 600	78.8	?
SnO_2		78.77	0.0

[a] The compositions given for the substances designated by Roman numerals here and in Figure 1 are experimental values; those for the corresponding proposed empirical formula are calculated.

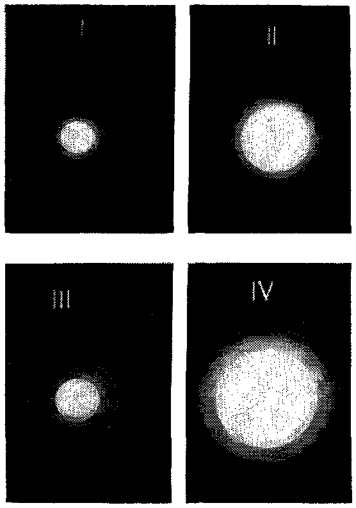

Figure 2.—Electron micrographs of the powders produced by dehydration of $Sn(OH)_4$. The numerals I–IV refer to the compositions designated in Figure 1.

Electron Diffraction.—The electron diffraction powder patterns are reproduced in Figure 2 for dehydration stages I, II, III, and IV. The micrographs clearly indicate the presence of different crystalline substances. The relative intensities of the diffraction lines were estimated visually from the film, and the *d* distances were calculated from the positions of the lines. The results are summarized in Table II. The measured lines are well defined and the *d* values are quite accurate. The micrographs leave little doubt that the

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TABLE II

THE d DISTANCES OF PRODUCTS I–IV, CALCULATED FROM THE ELECTRON DIFFRACTION PATTERNS OF FIGURE 2, AND THE VISUALLY ESTIMATED RELATIVE INTENSITIES[a] OF THE LINES

d, A	Intens	d, A	Intens	d, A	Intens	d, A	Intens
I		II		III		IV	
2.147	4	1.273	1	3.729	3	1.717	4
2.122	2	1.197	1	2.664	4	1.661	3
1.607	1	1.389	3	2.105	2	1.500	2
1.153	0	1.059	0	1.892	0	1.410	2
		0.977	0	1.419	2	1.295	2
		0.924	1	1.135	1	1.218	1
II		0.870	1			1.200	0
1.978	1	0.764	2	IV		1.147	1
1.764	1	0.721	0	2.390	3	1.106	0
1.416	4	0.700	0	1.990	4	1.024	0
1.346	2	0.683	0	1.892	2	0.989	0

[a] The visual, relative intensity scale is: 4, >80%; 3, 60–80%; 2, 40–60%; 1, 20–40%; 0, <20%, with a transparent film taken to be 0% and a black, completely exposed film as 100%.

substances are crystalline. However, the crystal systems with which we are dealing are unknown, so quantitative interpretations of the d values in terms of lattice parameters cannot be given.

Nuclear Magnetic Resonance.—The temperature dependence of the second moment M_2 of the proton magnetic resonance absorption is given in Figure 3 for I and II, the first and second dehydration stages. Also, the line shapes found for these two substances at low temperatures are shown in Figures 4 and 5, respectively, in the recorded form of first-derivative curves. In the case of III and IV, the absorption intensity was low, due partially to the decreased hydrogen concentration and in part to the resulting longer spin-lattice relaxation times. An approximate value of 2.5 gauss^2 was obtained for the second moment in III at 80°K, but the poor signal-to-noise ratio discouraged more detailed studies of III or IV. The interpretation of these results for I–III is approached in the same manner as that used in a similar study of several hydrated forms of uranium trioxide.[15–17]

We consider first the results for I. It is clear from Figure 3 that some motional narrowing of the absorption line may occur at the lowest temperature of measurement and that the 25.8 gauss^2 found for M_2 is probably less than the "rigid lattice" value. Nonetheless, this result and the line shape enable us to eliminate some of the possible proton configurations. The experimental line shape for I at low temperature, given in Figure 4, is inconsistent with a simple hydrate structure such as $SnO_2 \cdot H_2O$. The dashed line in Figure 4 is a theoretical curve calculated from formulas developed by Pake[15,18] for a pair of protons, with an intrapair distance of 1.595 A, a value not unreasonable for hydrates,[19] and with a broadening factor $\beta = 1.8$ gauss also appropriate for a simple hydrate.[15–19] The comparison of theoretical and observed line shapes is complicated by the residual motional narrowing possible in the latter. However, the 28-gauss^2 second moment of the theoretical curve is quite close to the experimental 25.8 gauss^2, even though the line shapes disagree very drastically. Therefore, it seems safe to conclude that I is not simply $SnO_2 \cdot H_2O$. On the other hand, it is unlikely that the protons occur in relatively isolated OH groups. A reasonable distance of closest approach for two OH groups would be about 2.5–3.2 A for such hydroxides. The second moment calculated for these circumstances[16] amounts to about 3–5 gauss^2, much less than that observed.

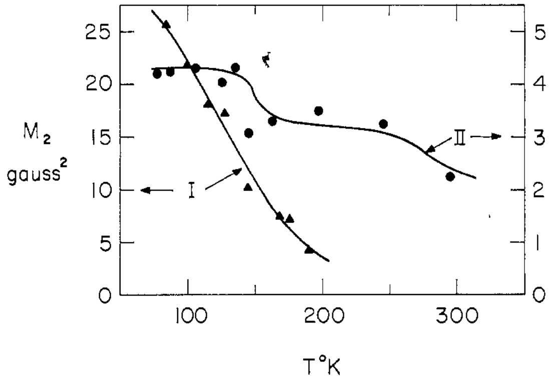

Figure 3.—The second moment M_2 in gauss^2 of the proton magnetic resonance absorption observed as a function of temperature for dehydration products I (SnO_3H_2) and II ($Sn_2O_5H_2$).

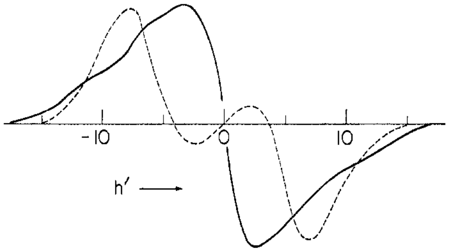

Figure 4.—The first derivative of the proton magnetic resonance absorption of I (SnO_3H_2) at 84°K, as a function of h', the displacement in gauss of the applied magnetic field from the 6325-gauss value at the center. The solid line is the observed curve; the dashed line is that calculated for relatively isolated H_2O molecules.

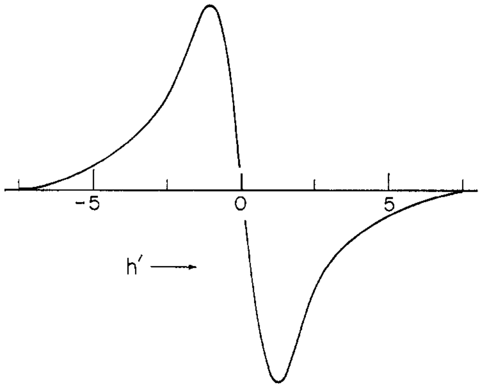

Figure 5.—The first derivative of the proton magnetic resonance absorption of II ($Sn_2O_5H_2$) at 80°K, observed as a function of h', the displacement in gauss of the applied magnetic field from the 6325-gauss value at the center.

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Another possibility which can be rejected is a hydrated hydroxide structure such as $Sn_2O_3(OH)_2 \cdot H_2O$, with the H_2O and Sn–OH protons occurring in relatively isolated sets. For this case, the line shape would be the sum of the dashed curve for H_2O in Figure 4 and a narrow central component[15] for the Sn–OH groups; the second moment would be only about 16 gauss^2, the average of 28 gauss^2 for the H_2O protons and 3-5 gauss^2 for the Sn–OH. The observed line shape is too broad and the M_2 is too large to fit this model. We conclude that the protons must be grouped together relatively closely in "clusters" of at least three and perhaps four or more.

The details of the "cluster" are less certain, but some speculation seems justified. The line shape for an equilateral three-spin system[20-22] bears little resemblance to that observed. However, the protons in such triangular groups could have[23] a rigid-lattice M_2 of as much as 31 gauss^2, and a cluster consisting of an OH proton close to a triangular proton group is consistent with the results. Also, it might account for the unusually wide temperature interval of $\gtrsim 100°$ over which the motional narrowing occurs, in that chemical exchange and diffusion could be involved as well as rotational motions. Nonetheless, an equally good explanation of the available data could be based on a structure having an H_2O close to two Sn–OH groups.

We turn next to the results for II. The low-temperature second moment is unchanged over a range of 60°, as given in Figure 3, so the value of 4.2 gauss^2 at 80°K is taken to be that of the rigid lattice. This value for M_2 and its temperature dependence are very similar to the results for β-UO_3H_2O which was shown to be[16] uranyl hydroxide, $UO_2(OH)_2$. We conclude that in II, the protons find themselves primarily in relatively isolated Sn–OH groups, in a structure which may be formulated as $Sn_2O_3(OH)_2$. There is some evidence, however, in the low-temperature line shape shown in Figure 5 that the material may not be entirely homogeneous. The "tails" of the derivative curve are relatively long, so long in fact that the line shape could not be fitted by the procedure employed successfully for $UO_2(OH)_2$.[16] The calculated line was always somewhat narrower than that observed, although there was good agreement in the center. These theoretical line shapes were calculated on the basis of a gaussian distribution of protons about a particular pair, which is a reasonable assumption for many compounds. It is possible, of course, that II is homogeneous with the line shape due to each proton having, say, two or three near neighbors instead of one. However, the tails in the line shape of II correspond to the maxima in the line shape of I, and it seems likely that the line shape in Figure 5 reflects incomplete conversion of I to II.

The low-temperature second moment of II lends support to the "cluster" structure proposed for I. The proton concentration in II is half that of I; thus, a uniform distribution of protons in both would lead to a reduction of M_2 for II to one-fourth that for I. However, the reduction factor is $\lesssim 4.2/25.8 = 1/6$, which implies not only that the protons are clustered, but also that the dehydration causes the loss of specific structural elements from each cluster.

Insofar as III is concerned, little can be said other than the fact that the low-temperature second moment of $\sim$2.5 gauss^2 is again substantially less than would be predicted on the basis of the measured decrease in proton concentration, if the protons were uniformly distributed in both II and III. However, it is what one would expect if II contained some I, so that the dehydration product became III which still contained some II.

In conclusion, although our studies have not answered all questions about the dehydration process nor provided a detailed description of the products, a self-consistent qualitative model has emerged. The dehydration proceeds *via* crystalline stages which are well defined, though somewhat overlapping. The first product may be formulated as $Sn_2O_3(OH)_2 \cdot H_2O$ with the qualification that the protons occur in clusters of three or four. The H_2O molecule in this substance is lost in the second dehydration step leaving most protons in well-separated Sn–OH groups. Accordingly, the subsequent dehydration is more difficult and less well understood.

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