



Chemical Reactions with White and Gray Tin

Theodore Gela

Citation: The Journal of Chemical Physics **24**, 1009 (1956); doi: 10.1063/1.1742667 View online: http://dx.doi.org/10.1063/1.1742667 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/24/5?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in Shubnikov-de Haas effect in thin epitaxial films of gray tin Appl. Phys. Lett. **55**, 2643 (1989); 10.1063/1.101961

Transformation Studies of Gray Tin Single Crystals J. Appl. Phys. **31**, 1973 (1960); 10.1063/1.1735482

On the Quality of Gray Tin Crystals and Their Rate of Growth J. Appl. Phys. **29**, 1110 (1958); 10.1063/1.1723369

Gray Tin Single Crystals J. Appl. Phys. **29**, 1007 (1958); 10.1063/1.1723351

GermaniumStabilized Gray Tin J. Appl. Phys. **25**, 1436 (1954); 10.1063/1.1721582



Chemical Reactions with White and Gray Tin

THEODORE GELA Stevens Institute of Technology, Hoboken, New Jersey (Received June 6, 1955)

Each of the two polymorphic forms of pure tin were found to produce different chemical compounds when reacted with concentrated hydrochloric acid under identical conditions. These findings were established by x-ray diffraction and chemical analysis. The metallic form of β white tin combined as Sn⁺⁺, whereas the semiconducting form of α gray tin combined as Sn⁺⁺⁺⁺. This chemical behavior was found to be consistent with the electronic configuration of the valence electrons ascribed to each form of the tin atom.

INTRODUCTION

'IN is polymorphic and can be transformed from the white β tetragonal to the gray α diamond cubic form at low temperatures. The transition temperature has been reported¹ to be 13.2° C and the latent heat of transformation² is 540 cal/mole at this temperature.

The electronic configuration of an α tin atom can be considered to consist of four bonding electrons in the uppermost quantum energy states and the transition to a β tin atom is accompanied by the dropping of one electron from the 5p to 5s state. When this occurs the β Sn atom has an electron pair in the 5p state leaving a vacant orbital in the 5s state. In accordance with Pauling's³ concept of the metallic bond a valence of 2.5 is ascribed to the β Sn. The α Sn, which is nonmetallic, is considered to be solely tetravalent.

When the transformation of β to α Sn occurs, and it occurs very slowly, there are significant changes in the physical properties related to the electronic behaviors, such that the β Sn exhibits metallic properties whereas the α Sn has semiconducting properties. Further, it is possible to classify α Sn in the same category with Si and Ge on the basis of the similarity in crystal lattice, valency and semiconducting behavior. It is significant, however, that the energy between the valence and conduction bands is 0.1 ev for α Sn and the values for Si and Ge are considerably greater.

Due to the differences in electronic behavior between the β and α forms of tin, it appears to be of interest to determine whether different chemical compounds can be obtained by reacting each form of tin under the same conditions.

EXPERIMENTAL PROCEDURES

An investigation was carried out to determine how each form of tin reacts chemically when dissolved in concentrated hydrochloric acid (37%) at -17° C for one week and subsequently crystallized by evaporation at 20°C.

Precautions were taken during the reactions so that the temperature did not vary from -17° C by more than

 $\pm 2^{\circ}$ C. This temperature was chosen because it could be maintained conveniently by refrigeration and furthermore it has been reported⁴ that β Sn will not transform to α Sn at this temperature, to any detectible degree, in less than about 1000 hours.

These reactions were repeated with especial consideration being given to the possible effect that absorbed oxygen⁵ might have in the reactions. Nitrogen was bubbled through the solutions for two hours from the start in order to free the solution from dissolved oxygen. The qualitative chemical tests on the products showed that there was no difference in the products formed in the initial and rerun tests.

The analytical techniques employed were by x-ray diffraction patterns on Geiger counter spectrometer traces, and by standard qualitative reactions of the compounds.



FIG. 1. These portions of the x-ray diffraction patterns for Samples A and B cover the same range of Bragg angles. The patterns show an obvious difference in the crystalline lattice in each product which resulted from the reactions of β white and α gray tin under identical conditions.

¹E. Cohen and A. Van Lieshaut, Z. physik. Chem. 137A, 1 (1935)

J. Brønsted, Z. physik. Chem. 88, 479 (1914).

³L. Pauling, Phys. Rev. 54, 899 (1938).

⁴ U. S. Army Signal Corps; Contract No. W 36-039-Sc-38135, p. 154 (November 1950). ⁶ J. W. Mellor, Modern Inorganic Chemistry (Longmans Green

and Company, New York, 1927), p. 970.

TABLE I. X-ray Geiger counter spectrometer determinations of: (A). White β Sn dissolved in HCl(37%) at -17°C and crystallized; and (B). Gray α Sn dissolved in HCl (37%) at -17°C and crystallized.

Samr	CoK	α radiati SnCl ₂ ASTM	on —Fe2(•2H2O I card lex)₃ filter −50 KV − Sample B		6 ma SnCl ₄ -5H ₂ O ASTM card index	
Intpl.	Rel.	Intpl.	Rel.	Intpl.	Rel.	Intpl.	Rel.
Sp.	Int.	Sp.	Int.	Sp.	Int.	Sp.	Int.
A^0	I/I_1	$A^{\mathfrak{o}}$	I/I_1	A٥	I/I_1		I/I_1
4.61	82	4.72	57	6.279	60		
3.97	100	4.00	71	6.181	90	6.2	100
3.555	88	3.60	100	5.988	100		
2.978	100	3.01	40	5.80	50		
2.790	68	2.82	40	5.295	100	5.3	48
2.525	100	2.58	71 -	5.019	30	5.0	20
2.412	21	2.41	57	4.233	30	4.21	8
2.301	21			3.920	30	3.96	20
2.261	59	2.24	23	3.737	40	3.70	6
2.211	47			2.948	70	2.94	28
2.178	47	2.16	40	2.768	50	2.76	16
2.118	74	2.07	40	2.648	80	2.64	24
				2.529	50	2.52	16
				2.352	20	2.35	10

The differences in the crystalline structures are readily apparent in the x-ray diffraction patterns, portions of which are reproduced in Fig. 1. The results of the x-ray diffraction analyses are given in Table I, together with comparisons of standard data from the Am. Soc. Testing Materials Card Index File,⁶ and these are as follows:

Analyses of the x-ray diffraction studies presented in Table I show that Sample A has the same structure as that published for $SnCl_2 \cdot 2H_2O$ whereas Sample B has the structure as that published for SnCl₄·5H₂O. The comparisons of the interplanar "d" spacings and relative intensities are within the normal range of experimental errors for such determinations.

In order to further test the validity of these findings, some qualitative chemical analyses7 of the compounds were performed with the results given in Table II.

The reactions in Table II were rerun under identical conditions using standard technical grade samples of

TABLE II. Results of qualitative analyses.

Samples	Reactants	Identifications
A. β Sn dissolved in HCL(37%) at -17° C with	oxalic acid	White crystalline precipitate of SnC ₂ O ₄
B. α Sn dissolved in HCL(37%) at -17° C with	oxalic acid	No precipitate
A. β Sn dissolved in HCL(37%) at -17°C with	NaOH+heat	Black oxide SnO
B. α Sn dissolved in HCL(37%) at -17° C with	NaOH+heat	White oxide SnO2

⁶ Am. Soc. Testing Materials Index of x-ray diffraction data, Publ. No. 48-B, Philadelphia, 1950. ⁷ E. K. McAlpine and R. A. Soule, *Qualitative Chemical Analysis*

(D. Van Nostrand Company, Inc., New York, 1933), pp. 224-225.

SnCl₂·2H₂O and SnCl₄·5H₂O. The results were precisely the same as obtained for Samples A and B.

Quantitative chemical analyses were made to determine the distribution of valence states in each of the reacted samples. Titrations were made by iodometry using a standardized 0.1NK103 solution⁸ in a CO₂ atmosphere. The results are shown in Table III.

The presence of some stannic ion in Sample A most likely resulted in partial oxidation during the time interval that it was sent to an outside laboratory to be analyzed. Accordingly, no particular physical significance is attached to its presence in A. These results substantially confirm the previous findings that the Sn^{++} predominantly is present in Sample A and the Sn^{++++} only is present in Sample B.

DISCUSSION

The possible reactions of each polymorphic modification of tin may be written down in four ways, according to:

$$\beta \operatorname{Sn}+2\operatorname{HCl} \cong \operatorname{SnCl}_2+\operatorname{H}_2$$
 (I)

 α Sn+2HCl \Rightarrow SnCl₂+H₂ (II)

$$\alpha \operatorname{Sn}+4\operatorname{HCl} \cong \operatorname{SnCl}_4+2\operatorname{H}_2$$
 (III)

 β Sn+4HCl \equiv SnCl₄+2H₂. (IV)

TABLE III. Results of titrations.

Samples	Stannous tin as SnCl2	Stannic tin as SnCl ₄
A. β Sn dissolved in HCL(37%) at -17° C	85.6%	14.4%ª
B. α Sn dissolved in HCL(37%) at -17° C		100%ь

* Calculated from total tin on dry basis (moisture present).

In order to determine which of these reactions will take place spontaneously, it is necessary to know the standard free energy change for each reaction. The present state of the available data is not adequate to make these calculations. Therefore, some likely reaction mechanism can only be suggested on the basis of the unique experimental results.

The data from Bichowsky and Rossini⁹ show that the heats of formations interpolated to $T=291^{\circ}K$ (18°C), for the two tin chlorides are substantially the same. Furthermore, the standard free energy change¹⁰ $\Delta F_{\mathrm{Sn}}^{\beta \to \alpha} = -0.06 \text{ kcal/mole at } T = 256^{\circ} \mathrm{K}(-17^{\circ} \mathrm{C}) \text{ is}$ quite small, so that the spontaneity of reactions (I) and (II) as well as (III) and (IV) would appear equally

⁸ Lundell, Hoffman, and Bright, Chemical Analysis of Iron and

Steel (John Wiley and Sons, Inc., New York, 1951), p.119. ⁹ F. R. Bichowsky and F. D. Rossini, The Thermo-Chemistry of Chemical Substances (Reinhold Publishing Corporation, New York, 1936), pp. 255–256.
¹⁰ L. E. Steiner, Introduction to Chemical Thermodynamics (McGraw-Hill Book Company, Inc., New York, 1948), p. 327.

probable. However, the experimental findings show The studies on tin, having a purity of 99.997%, demonstrate that each of the two polymorphic forms reacts with concentrated hydrochloric acid at $-17^{\circ}C$

that only (I) and (III) take place. Although these observations are not sufficient criteria for the quantitative free energy changes for the reactions, there remains a possibility that such data would not be able to differentiate between the likelihood of (I) and (II) as well as (III) and (IV). This being the case, it would appear reasonable that reaction paths may take place by activation processes governed principally by the initial electron energy state for each form of tin in the β and α states.

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 24, NUMBER 5

its transition temperature of 13.2°C.

SUMMARY

to produce different chemical compounds, notably, one

in which the white β tin combines as Sn⁺⁺ and the gray

 α tin combines as Sn⁺⁺⁺⁺. Therefore, it appears likely

that very interesting new compounds can be formed

with the reaction of gray α tin, providing the heat of

reaction does not cause the temperature to rise above

MAY, 1956

Zeeman Quadrupole Spectra of p-Chloroaniline and p-Chlorobenzylchloride*

HARLAN C. MEALT

Mallinckrodt Chemical Laboratory, Harvard University, Cambridge 38, Massachusetts

(Received July 22, 1955)

Analysis of the Zeeman quadrupole spectra of Cl^{35} in single crystals of *p*-chloroaniline and *p*-chlorobenzylchloride yields the following information: There are two sets of chlorine atoms in the *p*-chloroaniline crystal with differently oriented electrical field gradients. The angle between the field gradient z-axes is $79^{\circ}\pm1^{\circ}$; the y-axes are parallel. Both field gradients have the same asymmetry, $\eta = 0.06 \pm 0.03$. In *p*-chlorobenzylchloride there are four sets of chlorines (attached directly to the ring) which have differently oriented field gradients. The z-axes are parallel to the edges of a rectangular pyramid with apex angles of 8° and 67° , both $\pm 1^{\circ}$. All four have the same asymmetry, $\eta = 0.07 \pm 0.02$.

The bond between the chlorine and the ring is calculated to have $2.0 \pm 1.0\%$ double bond, $79 \pm 10\%$ single bond and $19\pm10\%$ ionic character in p-chloroaniline; $2.4\pm0.7\%$ double bond, $80\pm10\%$ single bond and $17 \pm 10\%$ ionic character in p-chlorobenzylchloride. The large uncertainty in the single bond and ionic characters results from the uncertainty in the hybridization of the chlorine bonding orbital.

I. INTRODUCTION

HE magnitudes and directions of the principal electrical field gradient components at a quadrupolar nucleus may be obtained from the measurement of the effect of a magnetic field on the quadrupole absorption of a single crystal. These quantities yield information about molecular bonding and orientation in the solid state. From the directional information obtained one may set a minimum on the number of molecules in the unit cell of the crystal and determine their orientation even in the absence of x-ray crystallographic data. Coupled with optical or other data which give the orientation of the crystal axes in the same crystal sample this new information may be of valuable assistance in analyzing x-ray diffraction patterns.

From the three principal field gradient components one can estimate the character of the bonding between the quadrupolar nucleus and its neighbors.1 If the nuclear spin is different from three halves these components may be obtained from the pure quadrupole

* The research reported in this paper was made possible by support extended Harvard University by the Office of Naval Research under Contract N5ori 76, Task Order V.

[†] Present address: Johns Hopkins University, Operations Research Office, 7100 Connecticut Avenue, Washington, D. C. ¹ C. H. Townes and B. P. Dailey, J. Chem. Phys. 20, 35 (1952).

absorption spectrum although no directional information is obtained. For spin $I=\frac{3}{2}$ only the largest component can be determined in this way and any uncertainty in the field gradient asymmetry, which must be estimated from other data, results in an uncertainty in this measurement. This error is ordinarily small enough so that good estimates of the covalency of many bonds involving such nuclei may be made. The asymmetry of field gradients at nuclei with spin $I=\frac{3}{2}$ can be determined in the solid state only if the Zeeman quadrupole spectrum is analyzed.

The method requires a single crystal as the absorbing sample. Also, if the unit cell is complex, the Zeeman spectrum may be so complex or of such low intensity that analysis is impossible. These difficulties limit the applicability of the method.

II. THEORY

Dean² has used the Zeeman quadrupole spectrum to estimate the directions and magnitudes of the principal electrical field gradient components at the chlorine nuclei in p-dichlorobenzene. He has given the details of the spectrum and the technique of analyzing it for ² C. Dean, Phys. Rev. 86, 607(A) (1952); Phys. Rev. 96, 1053 (1955).