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RADIOLYTIC PREPARATION OF ANHYDROUS TIN(II) CHLORIDE

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SUMMARY

Anhydrous tin(II) chloride ($SnCl_2$) is prepared by radiolysis with high energy electrons of a tin(IV) chloride ($SnCl_4$) solution in heptane. The $SnCl_4$ is reduced to insoluble $SnCl_2$. The energy yield, G($SnCl_2$), molecules of $SnCl_2$ produced per 100 electron volts, increases with $SnCl_4$ concentration from 1.6 at 0.15 molar $SnCl_4$ to 3.1 at 3.0 molar $SnCl_4$. Other parameters such as temperature (0° and 20° C), total dose (0.10 to 0.20 coulomb) and beam current (5 to 20 μA) have little influence on G($SnCl_2$). The method may be used to prepare other metal halides if the higher valence, more covalent metal halide is soluble in aliphatic hydrocarbons and the lower more ionic metal halide is insoluble.

The reaction mechanism is discussed; the radiolysis of both heptane and $SnCl_4$ is involved. At high $SnCl_4$ concentration G($SnCl_2$) appears to be limited by the yield of $SnCl_3$ radicals.

INTRODUCTION

For several years our interest has been directed toward the use of radiation (e.g., high energy electrons from a linear accelerator) in preparative chemistry. Because of the broad scope of this field we have recently published a review concerning possible applications of radiation to preparative chemistry (ref. 1). One particularly useful and interesting application of radiation chemistry discussed in this review is the synthesis of anhydrous lower valence metal halides; it involves the radiolysis of a solution of the higher valence metal halide in an appropriate organic liquid. One such preparation (refs. 1 and 2) that resulted in a good yield of high purity product was the deposition of iron (II) chloride by irradiation with high-energy electrons of an iron(III) chloride solution in tetrahydrofuran. Another example is the preparation of copper(I) bromide by radiolytic reduction of a solution of copper(II) bromide in 1-butanol (ref. 2). Because of the importance of anhydrous metal halides in a number of industrial applications, such as the use of divalent tin halides in electric arc lamps (ref. 3) and because of the interest in the lower valence halides of titanium as catalysts for the polymerization of unsaturated monomers (ref. 4), we have explored in some detail a radiolytic method that may be applied to the synthesis of these halides.

Presented in this report is a systematic study of the preparation of anhydrous tin(II) chloride; it involves the radiolytic reduction of tin(IV) chloride in heptane solution. Because of the lesser covalent character of the lower oxidation state tin halide, tin(II) chloride is insoluble in the hydrocarbon and is easily removed as a precipitate. Characteristic of the pure heptane-tin(IV) chloride system is that it contains no combined oxygen. Also, these solutions are self-dehydrating, in that small amounts of water which may be present are removed by hydrolysis of the tin(IV) chloride with the formation of an insoluble hydrolysis product. This undesired product may be conveniently removed by centrifugation and decantation before the radiolysis is begun. These inherent properties of the system lend themselves to the synthesis of oxygen free anhydrous tin(II) chloride.

The effect of temperature, total dose, dose rate, and tin(IV) chloride concentration on tin(II) chloride is presented. Of these parameters only the tin(IV) chloride concentration is found to have a significant effect on product yield. This dependence forms the basis for the discussion of the mechanism proposed for the process. In addition, the tin (II) chloride purity and comments as to causes of product contamination are given. The final section deals with the application of the method to the synthesis of metal halides other than tin(II) chloride.

EXPERIMENTAL

A good grade of commercial heptane (boiling point, 96° to 97° C) stored over Drierite was used to prepare the $SnCl_4$ solutions (0.15 to 3.0 M). These solutions were made by adding a known amount of anhydrous, fuming (certified) $SnCl_4$ to heptane in an Erlenmeyer flask containing a magnetic stirrer. The flask was immediately stoppered, and the mixture was stirred for several minutes to effect solution. The solution was then centrifuged to remove small amounts of insoluble material such as may be formed due to the hydrolysis of the $SnCl_4$. The clear liquid, total volume 500 milliliters, was decanted into the reaction vessel (fig. 1).

For irradiation 2-million-electron-volt electrons from a Dynamitron accelerator were used (ref. 5). For most experiments a beam current of 20 microamperes and a total dose of 0.15 coulomb were used. The reaction vessel and general procedure are described in more detail in earlier reports (e.g., ref. 6). To summarize, the solution was agitated during irradiation by passing an unreactive gas such as argon through a glass frit at the base of the reaction vessel. The contents of the vessel were maintained at 20° or 0° C during irradiation by immersing the vessel in a thermostatically controlled alcohol-water bath.

After irradiation the precipitated $SnCl_2$ (about 10 to 20 g) was removed by centrifuging and decanting the heptane containing unreacted $SnCl_4$ in solution. The $SnCl_2$ was washed twice with hot toluene and filtered on a sintered glass filter. Because of the sensitivity of the freshly prepared $SnCl_2$ to atmospheric oxidation and its hydroscopic nature, the $SnCl_2$ in the filter was not allowed to dry; instead the $SnCl_2$, still wet with toluene, was transferred to a drying tube and dried in vacuum at 100° C for about 10 hours. The dried $SnCl_2$ was then transferred as quickly as possible to a stoppered weighing bottle, weighed, and analyzed immediately. The product was analyzed by both X-ray diffraction and iodometry.

RESULTS AND DISCUSSION

Purity of $SnCl_2$

X-Ray diffraction of the $SnCl_2$ samples indicated the presence of only anhydrous $SnCl_2$. The iodometric equivalent of the $SnCl_2$ ranged from 97.1 to 99.4 percent (table I); the major impurity content probably arose from the unreacted $SnCl_4$ in solution remaining adsorbed on the $SnCl_2$ precipitate. When the final concentration of the $SnCl_4$ was low (0.5 mole/liter) the iodometric equivalent of the product corresponded to a purity of at least 99 percent $SnCl_2$. Contamination of the $SnCl_2$ increased as more concentrated $SnCl_4$ solutions were used at the same total dose. At the maximum initial $SnCl_4$ concentration of 3.0 moles per liter (shown in table I), the iodometric equivalent corresponded to only 97.1 percent $SnCl_2$. Moreover, the observed darkening of the hot toluene used to wash the product is indicative of a Friedel-Crafts reaction product. This product probably originated from the reaction of hot toluene with unused $SnCl_4$ adsorbed on the freshly precipitated $SnCl_2$. In these cases a pink discoloration persisted in the final product after the vacuum drying operation. It is believed that this colored impurity is a major contaminant of the final $SnCl_2$ product. It is suggested that, to eliminate this contamination, the removal of $SnCl_4$ on the $SnCl_2$ precipitate be accomplished by refluxing with an aliphatic hydrocarbon (heptane) instead of by washing with hot toluene.

Yield of $SnCl_2$

As shown in table I, $G(SnCl_2)$ increases with $SnCl_4$ concentration, reaching the highest value of 3.1 molecules per 100 electron volts at the highest $SnCl_4$ concentration (3.0 mole/liter) used. Essentially no effect of total dose (0.10 to 0.20 coulomb) and beam current (5 to 20 μA) on energy yield, G($SnCl_2$), was observed; thus, these results are not tabulated. A slight increase in G($SnCl_2$) was noticed when the irradiation was done at 0° C instead of at 20° C (table I).

As shown in table I the yield G($SnCl_2$) doubles for a twentyfold increase from 0.15 to 3.0 molar initial concentration of $SnCl_4$. A more convenient representation of these data is given in figure 2, which shows an almost linear relation between G($SnCl_2$) and the square root of the average $SnCl_4$ concentration. Because a significant proportion of the $SnCl_4$, especially in the more dilute $SnCl_4$ solutions, is used up in the formation of $SnCl_2$, average concentrations instead of initial concentrations are a truer presentation of the data.

Reaction Mechanism

To understand the reaction processes involved in the radiolytic deposition of $SnCl_2$ from $SnCl_4$ in heptane solution, the mechanism for the radiolysis of both the hydrocarbon and the metal halide must be considered. As mentioned in a previous report (ref. 1), saturated aliphatic hydrocarbons are radiolytically reducing with respect to the solute. The radiolysis of the straight chain hydrocarbon n-butane has been studied in detail (refs. 7 and 8). Hydrogen is a major product in the radiolysis, G(total H_2) = 4.8 molecules of hydrogen per 100 electron volts. The reactions leading to hydrogen formation were investigated by determining the hydrogen yield in the presence of various hydrogen and electron scavengers. From these yields, the following primary processes and corresponding G values for hydrogen formation were formulated (refs. 7 and 8).

From direct excitation and ionization:

$$\text{n-}C_4H_{10} \begin{cases} \rightarrow H\cdot & 0.7 \text{ G value} \\ \rightarrow H\cdot^* & 1.4 \\ \rightarrow H_2 & 0.6 \end{cases}$$

From the reaction of the solvated electron (produced by radiation) with n-C_4H_{10} ion:

$$\text{n-}C_4H_{10}^+ + e^- \begin{cases} \rightarrow H\cdot & 0.5 \text{ G value} \\ \rightarrow H\cdot^* & 0.6 \\ \rightarrow H_2 & 1.0 \end{cases}$$

where H· is the hydrogen atom, $H\cdot^*$ is a precursor of nonscavengeable molecular hydrogen, and H_2 is a molecularly detached hydrogen molecule.

Based on this reaction mechanism, the reducing yield of product involving scavengeable hydrogen atoms corresponds to the sum of G(H·) = (0.7 + 0.5) = 1.2 from both direct excitation and neutralization. However, by consideration of the total scavengeable reducing species from irradiated n-butane (solvated electrons plus hydrogen atoms from direct excitation) the maximum reducing yield is G(reducing) = (2.1 + 0.7) = 2.8. The same reaction mechanism probably applies to the heptane (mainly n-heptane) used in our synthesis of $SnCl_2$; therefore, the corresponding yields of H·, $H\cdot^*$, and H_2 for n-butane and n-heptane should not differ significantly. If we assume that both the solvated electrons and scavengeable hydrogen atoms reduce $SnCl_4$, we would expect that a low $SnCl_4$ concentration, G($SnCl_2$) should be about 2.8/2 = 1.4. (Dividing by 2 is necessary because a valence change of 2 is encountered in reducing $SnCl_4$ to $SnCl_2$.) This is indicated in figure 2; the straight line plot of G($SnCl_2$) against $\sqrt{C}$ (where C is the $SnCl_4$ concentration) extrapolates to G($SnCl_2$) = 1.4 at zero $SnCl_4$ concentration. It should be noted that no implication in terms of reaction mechanism can be made at this time from the linear G($SnCl_2$) against $\sqrt{C}$ relation.

The increase of G($SnCl_2$) with $SnCl_4$ concentration, however, tends to emphasize the influence of the radiolytic decomposition of $SnCl_4$ rather than heptane on product yield. In accord with this idea, the maximum equivalent of reducing species formed in irradiated hydrocarbons, G(reducing) = 2.8 is too low to account for the relatively high yield of $SnCl_2$, G($SnCl_2$) = 3.1, which is equivalent to G(reducing) = 6.2.

By analogy with the radiolysis of cyclohexane solutions of phosphorus (III) chloride (ref. 9) and pure carbon tetrachloride (CCl_4) (refs. 10 and 11), primary process in the radiolysis of $SnCl_4$ may be represented as follows:

$$SnCl_4 \rightarrow SnCl_3^{\cdot} + Cl\cdot$$

The decay of the $SnCl_3$ radical could possibly occur by disproportionation

$$2SnCl_3^{\cdot} \rightarrow SnCl_2 + SnCl_4$$

or by dimerization of two $SnCl_3$ radicals followed by nonsymmetric decomposition of the dimer formed

$$2SnCl_3^{\cdot} \rightarrow (SnCl_3)_2 \rightarrow SnCl_2 + SnCl_4$$

The scavenging of the chlorine atom by the irradiated hydrocarbon may be comples and involves reaction with the scavengeable e^- and H·, hydrocarbon fragments, and/or hydrogen abstraction from the hydrocarbon to form hydrogen chloride (HCl). The insoluble $SnCl_2$ produced from the disproportionation of $SnCl_3$ radicals or from the decomposition of the $(SnCl_3)_2$ is, of course, precipitated. The radiolytic yield of CCl_3 radicals from CCl_4 is 7.0 ±0.2 (ref. 12), which is probably close to the yield of $SnCl_3$ radicals from the radiolysis of $SnCl_4$. A $G(SnCl_3^{\cdot})$ of about 7 is in accord with our maximum $G(SnCl_2)$ of 3.1, which corresponds to $G(SnCl_3^{\cdot}) = 6.2$. It appears then that the maximum value of $G(SnCl_2)$ at high $SnCl_4$ concentrations is limited by the $SnCl_3$ radical yield.

However, $G(SnCl_2)$ increases too slowly with $SnCl_4$ concentration (the yield doubled for a twentyfold increase in $SnCl_4$ concentration) to consider only the radiolysis of $SnCl_4$ in determining the yield of $SnCl_2$. Reduction of $SnCl_4$ and $SnCl_3$ radicals by the reducing species from irradiated heptane must be acknowledged as contributing to the yield $G(SnCl_2)$.

Application

With proper care in the handling of starting materials and product in an inert atmosphere (e.g., dry nitrogen), the radiolytic method presented here may be used for the synthesis of several oxygen free, anhydrous metal halides. The method is applicable to such preparations where the more covalently bonded higher valence metal halide is soluble in aliphatic hydrocarbons (e.g., heptane) and the reduced more ionic lower valence metal halide is insoluble. Thus, metal halides other than $SnCl_2$ may be prepared by this method; for example, irradiation of titanium(IV) chloride or tin(IV) iodide in heptane solution with high energy electrons should deposit anhydrous titanium(III) chloride and tin(II) iodide, respectively. It can be assumed that the same reaction mechanisms postulated for the radiolytic formation of $SnCl_2$ apply to the general preparation of metal halides by this method. The maximum yield of product at high metal halide concentrations would probably be limited by the yield of metal halide radicals from the reaction

$$MX_n \xrightarrow{\text{radiation}} \dot{MX}_{(n-1)} + X\cdot$$

where MX_n is the metal halide, $\dot{MX}_{(n-1)}$ is the metal halide radical, and $\dot{X}$ is a halogen atom.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, July 27, 1973,
501-21.

REFERENCES

1. Philipp, Warren H.: Survey of Application of Radiation to Preparative Chemistry. NASA TN D-7285, 1973.
2. Philipp, W. H.; Marsik, S. J.; May, C. E.; and Lad, R. A.: Use of Radiation in Preparative Chemistry. NASA TM X-67982, 1971.
3. Speros, D. M.; Caldwell, R. M.; and Smyser, W. E.: Thermodynamic and Kinetic Considerations Pertaining to Molecular Arcs. High Temp. Sci., vol. 4, no. 2, Apr. 1972, pp. 99-127.
4. Lenz, Robert W.: Heterogeneous Polymerization of Unsaturated Monomers. Organic Chemistry of Synthetic High Polymers. Interscience Publ., 1967, pp. 579-654.
5. Cleland, Marshall R.; and Farrell, Paul: Dynamitrons of the Future. IEEE Trans. on Nucl. Sci., vol. NS-12, no. 3, June 1965, pp. 227-234.
6. Philipp, Warren H.; and Marsik, Stanley J.: Radiation-Induced Reduction of Divalent Copper Salts in Solutions. NASA TN D-4451, 1968.
7. Shida, Shoji; Fujisaki, Noboru; and Hatano, Yoshihiko: Hydrogen Formation in the Radiolysis of Liquid n-Butane. J. Chem. Phys., vol. 49, no. 10, Nov. 15, 1968, pp. 4571-4575.
8. Fujisaki, Noboru; Shida, Shoji; Hatano, Yoshihiko; and Tanno, Kuniyasu: The Radiolysis of Liquid n-Butane. J. Phys. Chem., vol. 75, no. 18, Sept. 2, 1971, pp. 2854-2860.
9. Henglein, Arnim: Preparative Radiation Chemistry - II. The Reactions of Hydrocarbons with Phosphorus Trichloride and Other Inorganic Chlorides Under the Influence of High-Energy Electrons. Int. J. Appl. Rad. Isotopes, vol. 8, 1960, pp. 156-163.
10. Ambramson, Fred P.; Buckhold, Brenda M.; and Firestone, Richard F.: The Effects of Temperature and Various Solutes on the Radiolysis of CCl_4. J. Am. Chem. Soc., vol. 84, no. 12, June 20, 1962, pp. 2285-2288.
11. Chen, T. H.; Wong, K. Y.; and Johnston, F. J.: Radiolysis of Chloroform and Carbon Tetrachloride. J. Phys. Chem., vol. 64, no. 8, Aug. 1960, pp. 1023-1025.
12. Bibler, Ned E.: The Radiolysis of Carbon Tetrachloride. Radical Yields and the Formation of Tetrachloroethylene as an Initial Product. J. Phys. Chem., vol. 75, no. 1, Jan. 7, 1971, pp. 24-30.

TABLE I. - PREPARATION OF $SnCl_2$ FROM A HEPTANE SOLUTION OF $SnCl_4$

[Electron energy, 2 MeV; dose, 0.15 coulomb; beam current 20 μA; irradiation temperature 20° C unless otherwise specified.]

Initial $SnCl_4$ concentration, mole/liter	Energy yield, $G(SnCl_2)$, molecule/100 eV	Purity of $SnCl_2$ (iodimetric equivalent), percent	Final $SnCl_4$ concentration,[a] mole/liter
0.15	1.6	99.4	0.05
.30	1.9	98.8	.18
.50	2.1	98.6	.37
.70	2.2	----	.56
1.00	2.4	98.2	.85
1.50	2.6	----	1.3
2.0	2.8	97.6	1.8
3.0	3.1	97.1	2.8
.50	[b]2.2	----	.36
1.0	[b]2.6	----	.84

[a] Calculated from initial concentration and yield.
[b] Irradiations carried out at 0° C.

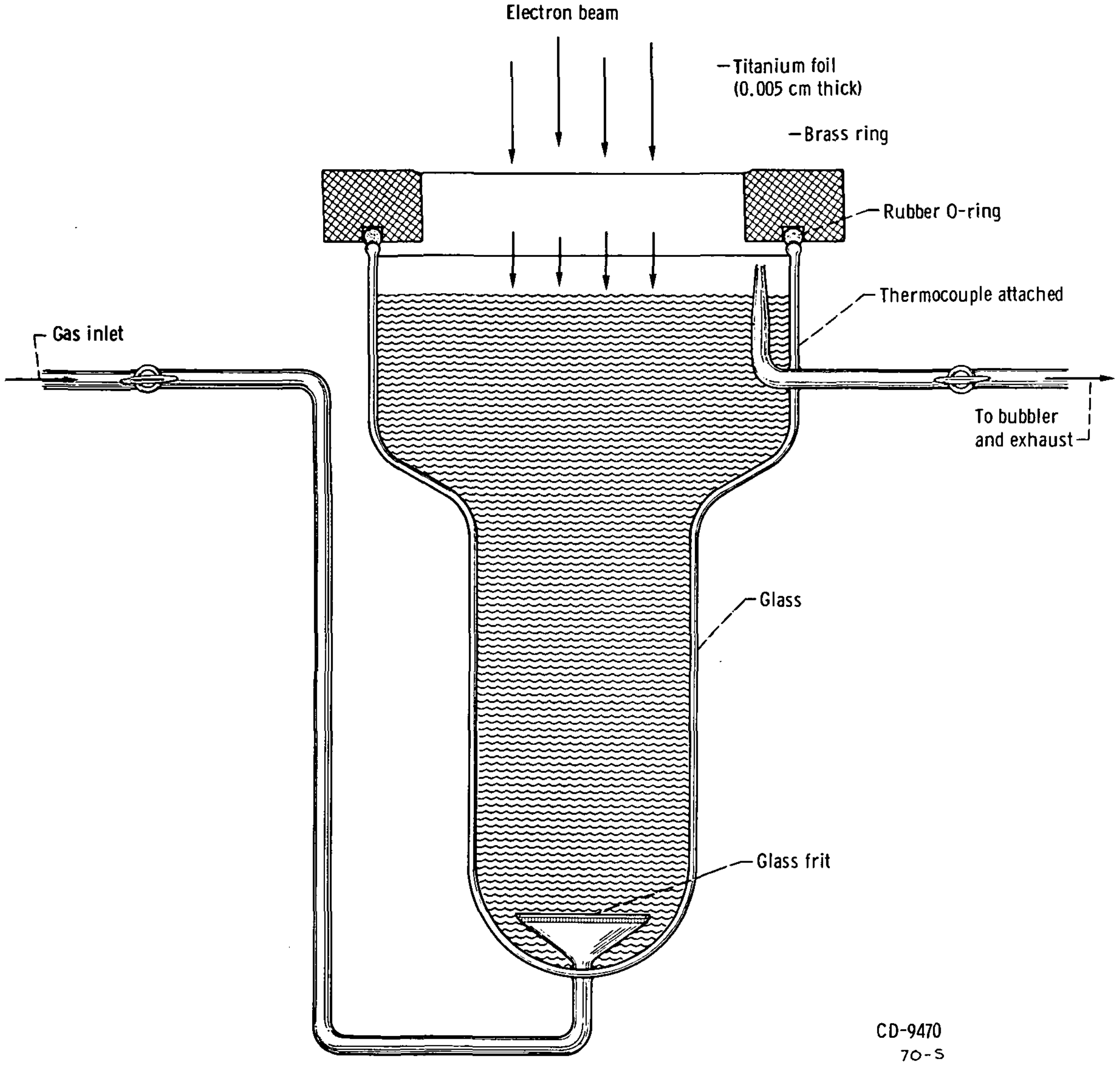

Figure 1. - Irradiation vessel.

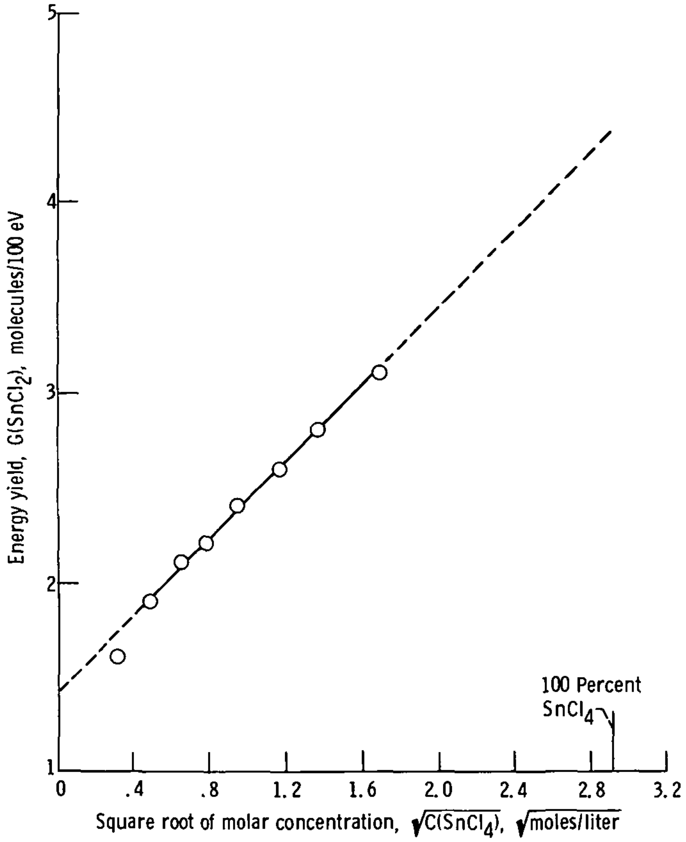

Figure 2. - Effect of $SnCl_4$ concentration on $SnCl_2$ yield.

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