

the absorption is over a much wider region. Allmand and Reeve³ found quantum efficiencies ranging from 0.01 at 265 $m\mu$ to 0.00095 at 365 $m\mu$. Possibly only the light absorbed by the carboxyl group causes decomposition, and apparently this lies in the region below 250 $m\mu$.

Summary

A further study is made of the photochemical decomposition of malonic acid and the results obtained are applied to the general process of photochemical decomposition of carboxyl groups. The effective light in this process seems to lie in the region 200–250 $m\mu$. Decomposition gives as products carbon dioxide and a hydrocarbon residue. Photochemical decarboxylations are characterized by low temperature coefficient, quantum efficiency near unity, low absorption of light. Presence of other absorbing groups in the molecule may modify these characteristics.

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GLACIAL ACETIC ACID AS A SOLVENT FOR THE ELECTRODEPOSITION OF METALS.^{1,2} AN X-RAY DIFFRACTION STUDY OF THE STRUCTURE OF DEPOSITS OF ARSENIC, ANTIMONY AND BISMUTH

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RECEIVED SEPTEMBER 11, 1931

PUBLISHED FEBRUARY 5, 1932

A considerable number of investigations have demonstrated that a variety of solvents may be employed for the electrodeposition of metals,^{2c} and in some instances these studies have shown that certain non-aqueous solvents may be employed with distinct advantage over water. A survey of solvents used for this purpose reveals that they are all either basic or amphiprotic in nature and that no definitely acidic solvent has yet been investigated. However, most compounds of such elements as arsenic, antimony, bismuth and stannic tin undergo considerable solvolysis in basic solvents and dissolve only in the presence of acids. The striking solubility of the chlorides of these elements in glacial acetic acid with the apparent non-formation, at least of insoluble, solvo-basic products, indicated immediately that it might be of considerable theoretical interest to study the discharge of these metallic cations from glacial acetic acid.

Glacial acetic acid has been shown to be an excellent ionizing medium

¹ This paper was presented at the Buffalo meeting of the American Chemical Society, September, 1931.

² For earlier papers of this series see (a) Yntema and Audrieth, *THIS JOURNAL*, 52, 2693 (1930); (b) Audrieth and Yntema, *J. Phys. Chem.*, 34, 1903 (1930); (c) Audrieth and Nelson, *Chem. Reviews*, 8, 335 (1931); (d) Audrieth, Jukkola, Meints and Hopkins, *THIS JOURNAL*, 53, 1805 (1931).

and, as Davidson³ has pointed out, may be regarded as the parent solvent of a system of acids, bases and salts. Because of its limited proteolytic activity it has been characterized as a very acidic solvent by Hall.⁴

No attempt has yet been made to determine the effect of change of solvent upon the character of metallic deposits. In their study of the electrodeposition of metals from liquid ammonia at -33° Audrieth and Yntema^{2b} regarded it as quite significant that tin was deposited as white tin rather than in the form of gray tin, the modification stable at that temperature. However, Cohen⁵ has pointed out that "most metals are electrodeposited in a metastable form," thus making it difficult to obtain suitable metallic plates except under very special conditions.

Cohen and Coffin⁶ have recently shown that concentration and temperature are the two factors which most profoundly affect the electrodeposition of antimony from strongly acidified aqueous solutions of the chloride. Changes in current density appear to be only of minor importance. Thus, at low temperatures and high concentrations the metastable or "explosive" modification is always deposited, whereas low concentrations and high temperatures favor the formation of the crystalline or stable form of the metal. These data suggested the advisability of studying the deposition of antimony from glacial acetic acid solutions to determine the effect of change of solvent. Cohen and Coffin used the appearance of the deposits as the basis for their conclusions, whereas the data given by the authors were determined by an x-ray diffraction study of the deposited metals.

Experimental⁷

Electrodeposition of Antimony from Glacial Acetic Acid.—Antimony can be deposited from glacial acetic acid solutions of the chloride over a wide range of experimental conditions at room temperatures. The concentrations of solutions were varied from 5 to 55 g. of antimony trichloride per 100 g. of solution, the current densities from 0.001 to 0.04 ampere per square centimeter. All experiments were carried out using a 110-volt direct current in series with a lamp-bank for variable resistance. The electrolytic cell was immersed in a constant temperature bath and fitted with a stirrer to prevent local impoverishment of antimony ions in the

³ Davidson, *Chem. Reviews*, **8**, 175 (1931).

⁴ Hall, *ibid.*, **8**, 191 (1931).

⁵ Cohen, "Physico-chemical Metamorphosis and Problems in Piezochemistry," Vol. I, George Fisher Baker Non-resident Lectureship Series, McGraw-Hill Book Co., Inc., New York, 1926, p. 44.

⁶ Cohen and Coffin, *Z. physik. Chem.*, Abt. [A] **149**, 417 (1930).

⁷ The authors wish to take this opportunity to acknowledge their indebtedness to Mr. Harlan W. Nelson and to Mr. Lionel H. Smith, who performed some of the preliminary experimental work involving the electrodeposition of metals from glacial acetic acid.

neighborhood of the cathode. Two anodes of pure antimony were used between which was placed the cathode.

Deposits of antimony at room temperatures are smooth and possess a black metallic luster. While fairly adherent at first, all of these plates tend in time to dust off and to become non-adherent. Solution of the original metal deposits in nitric acid and subsequent analysis showed that in all cases a considerable amount of antimony trichloride had been adsorbed, indicating that possibly the "explosive" or metastable form had been deposited. This supposition was subsequently verified, first, by comparing the deposits obtained from acetic acid with those obtained from acidified aqueous solutions of the chloride under conditions known to give the metastable modification,⁸ proving their macroscopic identity; second, by immersing thicker deposits in an oil-bath and heating slowly to 100°, at which temperature violent disruption of the antimony plates usually occurred.⁸

Attempts to discharge antimony at higher temperatures invariably resulted in the formation of black, pulverulent deposits. In general, deposits upon brass and copper were found to be more adherent than those upon platinum. The addition of water to the electrolytic bath, while not affecting the type of deposit, was found to lower very appreciably the resistivity of the solutions.

The effect of concentration and temperature on the structure of the deposits was investigated systematically for concentrations varying from 7.5 g. to 40 g. of antimony trichloride in 100 g. of solution, and temperatures varying from 20 to 65°. It was found that current density could be varied between 0.01 and 0.07 ampere per square centimeter without affecting the nature of the deposit. Consequently, no attempt was made to keep the current density absolutely constant. For all the data recorded in Fig. 1, however, the current density was kept at 0.03 ± 0.01 ampere per square centimeter. The antimony was deposited on copper, and the results given in Fig. 1 are therefore not strictly comparable with those of Cohen and Coffin,⁶ who used platinum as the base metal.⁹

The structure of the deposits was established by x-ray diffraction patterns. These offer more conclusive evidence than the tests described above, which were doubtful for many of the specimens examined. It has recently been shown that explosive antimony is amorphous,⁸ and when it explodes it changes to the usual rhombohedral form. There should be little difficulty in distinguishing the two forms by a mere inspection of their diffraction patterns.

⁸ Steinwehr and Schulze, *Z. Physik*, **63**, 815 (1930).

⁹ It was found difficult to obtain consistent results when platinum was used as the base metal. The reason for this is as yet unknown, although it is the authors' experience that antimony deposited from glacial acetic acid solution never adheres as well to platinum as it does to copper.

Powder patterns were obtained, using the General Electric Multiple Diffraction apparatus with Mo K_{α} radiation. The antimony was deposited on a 22-gage copper wire which was set in the regular specimen holder of the quadrant cassette, the diffraction pattern being produced by the reflection of x-rays from the surface of the specimen. It is essential, of course, that the diffraction pattern be obtained without disturbing the deposit. In all the cases the deposit was so thin that the pattern for copper was always present on the film. The time of exposure varied from twenty-four to forty-eight hours at 20 ma.

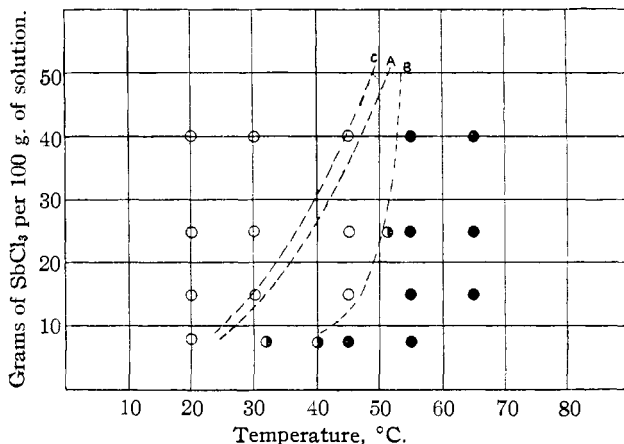


Fig. 1.—○, Amorphous; ●, crystalline; ◐, mixtures.

The diffraction pattern of the crystalline deposits was identified by direct comparison with the diffraction pattern for pure crystalline antimony. The absence of any lines other than those of copper indicates the presence of the explosive form, provided the following two sources of error have been considered. If a crystalline deposit is too thin, it will not give any diffraction pattern. This source of error was eliminated by heating all of the apparently amorphous deposits above the transition temperature to effect their change to the crystalline state. If a crystalline diffraction pattern is then obtained it indicates the sufficient thickness of the deposit and shows that the original deposit was amorphous.

It is well known that in an electrodeposited film the crystal grains usually exhibit preferred orientation with respect to the base metal. Such a condition might lead to an erroneous interpretation of the diffraction pattern, since it might happen that very few, if any, of the planes would reflect in the proper direction to be caught on the photographic plate. Bismuth films, reported in an earlier work to be amorphous, have recently been shown to be crystalline, but highly oriented,¹⁰ the error in the first

¹⁰ Büssel, Gross and Herrman, *Z. Physik*, **64**, 537 (1930).

interpretation arising as described above. In the present work error from this source was practically eliminated by reflecting the x-ray beam from the surface of a small wire. The degree of curvature is so great that even if the crystals were oriented with respect to the surface of the wire there would be sufficient variation of the orientation to the x-ray beam to insure reflection from many different planes.

Even with these precautions it was often impossible to state definitely whether the deposit was amorphous or crystalline. The presence of at least the two strongest lines of the antimony pattern was taken as evidence that the deposit contained crystalline material. A majority of the specimens examined were evidently mixtures of the two forms, since the complete diffraction pattern of antimony could be brought out by heating above the transition temperature a deposit whose original diffraction pattern showed only two or three of the strongest lines.

The results of this phase of the investigation are shown in Fig. 1. Curves C and A are those of Cohen and Coffin⁶ showing the effect of concentration and temperature on the structure of the deposits from aqueous solutions. These curves were determined for current densities of 0.02 and 0.05 ampere per square centimeter, respectively. Since the current density was maintained between these limits during deposition from glacial acetic acid, it is not a significant variable. Curve B indicates the results obtained using glacial acetic acid as the solvent. It appears that for a given concentration amorphous antimony may be deposited from glacial acetic acid at a higher temperature than from aqueous solution, the difference being marked at lower concentrations; while at a given temperature it may be deposited from solutions of lower concentration. The change in solvent apparently has one other effect. Cohen and Coffin imply that the change from amorphous to crystalline antimony is sharp, while in deposits from glacial acetic acid the two forms are mixed over a rather wide range. Only the specimens deposited under conditions furthest from the curve show evidence of being predominantly crystalline; and those indicated in the figure as mixtures contain only a small proportion of the crystalline form.

Deposition of Arsenic.—Conditions analogous to those employed in the deposition of antimony were used to effect the deposition of arsenic as a black, lustrous, metallic plate from solutions of the chloride in glacial acetic acid. There appeared to be no tendency toward the formation of "burnt" plates at higher temperatures as noted in the case of antimony. Arsenic trichloride is either very much less ionized, or less solvolyzed in acetic acid than antimony trichloride, since solutions of the former do not conduct as well as those of the latter of the same concentration.

x-Ray diffraction patterns were determined for deposits under extreme conditions of temperature and concentration comparable to those studied in the case of antimony. The method described for antimony was used for

obtaining the patterns and the same precautions were observed to make sure that deposits which gave an apparently amorphous pattern were truly amorphous. There was no question as to the sufficient thickness of these deposits since a film of arsenic could easily be peeled off in many cases, and the plate was often thick enough to prevent diffraction from the base metal. Amorphous diffraction patterns were obtained by transmission of the x-ray beam through a specimen which had been detached from the base metal and more or less broken up, thus definitely eliminating the possibility of an apparently amorphous pattern resulting because of the preferred orientation of the crystals of the deposit. Results of typical runs are given in Table I.

TABLE I
ELECTRODEPOSITION OF ARSENIC FROM GLACIAL ACETIC ACID

Concentration		Metal base	Current density amp./sq. cm.	Temp., °C.	Structure
G. AsCl ₃	G. HC ₂ H ₃ O ₂				
12.6	87.4	Cu	0.0006	26	Amorphous
12.6	87.4	Pt	.006	90	Amorphous
50	50	Cu	.008	26	Amorphous
50	50	Pt	.020	90	Amorphous

Two crystalline forms of arsenic are known and two amorphous forms have been described.¹¹ As in the case of antimony the change from amorphous to crystalline arsenic is monotropic and has been reported at about 270° or at 360°. One would expect to be able to control the nature of this deposit near this transition point, as in the case of antimony, by varying the concentration and temperature of the bath. This possibility will be investigated using solvents which will permit the maintenance of the desired temperature range.

Deposition of Bismuth.—Bismuth chloride is very much less soluble in glacial acetic acid than are the chlorides of antimony and arsenic. Electrolysis of such solutions results in the cathodic discharge of the metal, but only at low concentrations, low temperatures and low current densities can deposits be obtained which are smooth and adherent. Even under these conditions continued electrolysis results in the formation of a black

TABLE II
ELECTRODEPOSITION OF BISMUTH FROM GLACIAL ACETIC ACID

Concentration		Metal base	Current density, amp./sq. cm.	Temp., °C.	Structure
G. BeCl ₂	G. HC ₂ H ₃ O ₂				
6	94	Cu	0.011	28	Smooth
23	77	Cu	.022	29	Gray, powdery
33	67	Cu	.024	29	Gray, powdery
6	94	Pt	.028	95	Black, powdery
33	67	Pt	.026	95	Black, powdery

¹¹ J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, Vol. IX, 1929, p. 18.

spongy mass of metal. x-Ray diffraction patterns, obtained in the same manner as described above, indicate that within the limits studied bismuth is deposited as the crystalline metal. Table II gives typical results for bismuth.

Amorphous bismuth has not yet been reported. From analogy one might expect to electrodeposit the non-crystalline form from solvents permitting the maintenance of a much lower temperature.¹²

Summary

Arsenic, antimony and bismuth may be electrodeposited from solutions of their chlorides in glacial acetic acid.

x-Ray diffraction studies of these deposits indicate that, under the conditions of temperature and concentration studied, arsenic is always obtained in the amorphous form, whereas bismuth is discharged as the crystalline metal.

Antimony may be deposited in either the "explosive" metastable modification or in the crystalline form depending upon conditions of temperature and concentration.

These studies indicate that the solvent must be considered as an additional factor of importance among the conditions which affect the structure of electrodeposited antimony.

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¹² The chlorides of stannic tin, titanium, germanium and phosphorus are quite soluble in glacial acetic acid. Only in the case of tin is the resulting solution appreciably conducting to give a deposit of the metal upon electrolysis. Titanium tetrachloride appears to react with the solvent with formation of a white precipitate. Zinc chloride, though soluble, apparently does not ionize to any large degree in glacial acetic acid. The addition of water, however, increases the conductivity decidedly and leads to the deposition of zinc.