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The University of Oklahoma, Ph.D., 1962
Chemistry, analytical

University Microfilms, Inc., Ann Arbor, Michigan

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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

ONIUM - TYPE COMPOUNDS AS ANALYTICAL REAGENTS FOR ORGANIC ACIDS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

BY

ALVIS BERYL GAINER

Norman, Oklahoma

1961

ONIUM - TYPE COMPOUNDS AS ANALYTICAL

REAGENTS FOR ORGANIC ACIDS

APPROVED

Harold E. Affsprung

Brian E. Hoyle

P. C. Colbert

Bernard O. Heston

S. H. Wender

DISSERTATION COMMITTEE

ACKNOWLEDGMENT

The author wishes to express his deep appreciation to Dr. Harold E. Affsprung for suggesting the problem, for providing a research assistantship from funds made available to him, and for his counsel, encouragement, and patience during the course of this research. He would also like to express his gratitude to the National Science Foundation for providing funds which made possible these investigations.

The author wishes to thank the faculty and staff of the Department of Chemistry for their guidance, cooperation, and assistance.

He also wishes to express his appreciation to his fellow graduate students, whose fellowship and cooperation will long be remembered.

Finally, the author wishes to express his thanks and appreciation to his wife for typing the dissertation and for her patience and assistance during the course of his studies.

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ONIUM - TYPE COMPOUNDS AS ANALYTICAL REAGENTS FOR ORGANIC ACIDS

CHAPTER I

INTRODUCTION

The greater number of the organic reagents which are used in quantitative analysis are anions and are commonly used to extract or precipitate various cations. Only a few organic cations have been used, most of which are nitrogen-containing compounds. Recently, onium-type compounds, which contain as the central atom an element other than nitrogen, have been used as precipitation reagents. The purpose of this research is to develop an organic onium-type compound which will determine water soluble organic and inorganic acids by precipitation, selective extraction, direct titration, or a combination of these techniques.

Tetraphenylarsonium chloride, triphenyltelluronium chloride, tetraphenylphosphonium chloride, triphenyltin chloride, triphenylgermanium chloride, triphenylsulfonium chloride, triphenylselenonium chloride, diphenyl mercury, triphenyllead chloride or tetraphenyllead, and tetraphenylstibonium sulfate are the organic onium-type compounds, other

than the nitrogen-containing compounds, which have been reported for the determination of various inorganic anions. Some triarylsilicon and tri-, tetra-, and pentaphenylchromium compounds have been synthesized but have not been used as analytical reagents. Only tetraphenylstibonium sulfate (1) has been used for the qualitative determination of various organic anions. In general, most of the inorganic salts of the onium type cations mentioned above are too soluble to permit the determination of most inorganic anions by gravimetric analysis. For example, Matsuo and Shinagawa (37) state that triphenyltelluronium chloride is not suitable for use as an analytical reagent since the precipitates obtained with metal complex ions are too soluble.

The first onium-type compound used as an analytical reagent, however, was tetraphenylarsonium chloride. Although other onium-type compounds have been synthesized, tetraphenylarsonium chloride is probably the most widely used of all onium-type compounds which contains a metal as the central atom. This reagent was first prepared as the bromide salt by Blicke and Monroe (9) using the Grignard reaction. The starting materials were triphenylarsine oxide and phenylmagnesium bromide. Triphenylarsine has been prepared by the action of arsenic trichloride on phenylmagnesium bromide (51) and by the action of sodium and arsenic trichloride on chlorobenzene (54) or bromobenzene (40).

Willard and Smith (74) have shown that tetraphenylarsonium solutions can be standardized against triiodide solution by potentiometric titrations. The reaction was shown to be $(C_6H_5)_4As^+ + I_3^- = (C_6H_5)_4As\ I_3$ and when an equivalent quantity of triiodide has been added to the tetraphenylarsonium chloride solution there is a sudden large increase in the oxidation potential. The presence of free acid, except HNO_3, in moderate amounts does not interfere.

Lamprey (32) in 1935 showed that tetraphenylarsonium chloride could be used for the gravimetric determination of perchlorate, periodate, and the chloride complexes of gold and platinum. Willard and Smith (74) in 1939 reported the potentiometric titration of mercury, tin, cadmium, and zinc, all as the chloride complexes.

Potratz (56) used tetraphenylarsonium chloride for the spectrophotometric determination of cobalt and bismuth in uranium using an extraction technique. The spectrophotometric determination of cobalt as tetraphenylarsonium cobaltthiocyanate has been reported by Affsprung, Barnes, and Potratz (2). The method has been evaluated by Pepkowitz and Marley (50) and highly recommended not only for the determination of cobalt in steel but for the inconels, nickel, chromium, and boron carbide as well. Cobalt is separated from an aqueous solution by chloroform extraction of tetraphenylarsonium cobaltthiocyanate. In the pH range from 1.9

to 6.9 over 90% of the cobalt is removed in a single extraction. All interferences such as Fe^{+++}, Cu^{+2}, Mo^{+5}, Mo^{+6} which form colored extractable thiocyanate complexes can be removed by fluoride complexation. Neeb (45) has reported the spectrophotometric determination of osmium with tetraphenylarsonium chloride. 0.5 micrograms of osmium can be detected in the presence of a 300 fold excess of ruthenium. Os^{+4} forms a yellow precipitate with tetraphenylarsonium chloride in concentrated HCl solution and can be extracted with chloroform and determined spectrophotometrically. The procedure has also been extended to the determination of Pd, Pt, and Ir. Smith (66) has reported that thallium can be determined gravimetrically by precipitation with tetraphenylarsonium chloride from a hydrochloric acid solution containing the element in the trivalent state. Ducret and Seguin (22) have reported the use of tetraphenylarsonium chloride to precipitate traces of fluoborate ion and the subsequent determination of these traces by a spectrophotometric method after extraction by an organic solvent. Coursier, Hure, and Platzer (17) developed a chloroform extraction method for fluoborate ion. Beeston and Lewis (7) have reported the spectrophotometric determination of rhenium with tetraphenylarsonium chloride. The perrhenate precipitate is extracted from an aqueous solution at a pH of 8-9 with chloroform while any molybdenum present remains in the aqueous phase. Andrew

and Gentry (5) have reported the spectrophotometric determination of rhenium in W-Re and Mo-Re alloys. The perrhenate was extracted and the optical density of the chloroform extract was measured directly at 255 millimicrons with chloroform as the reference liquid. Ellis and Gibson (23) have reported the use of triphenylmethylarsonium thiocyanate in the microestimation of copper. The copper complex was twice extracted with o-dichlorobenzene, the combined extracts made up to 25 ml., and the absorption measured. Very few materials interfere.

Kolthoff and Johnson (31) reported the amperometric titrations of Sn(IV) and Hg(II) with tetraphenylarsonium chloride. For best results the chloride ion concentration should be maintained at approximately 3-4 M. The best range of acidity is between 2-4 N. The acidity can be lowered to 1N without seriously affecting the results, at a total chloride ion concentration of 2-3 N. The interfering substances are (a) those which give polarographic currents at -0.3 volts, (b) those which react with tetraphenylarsonium ion, and (c) those that complex tin to form ions which are not precipitated by the reagent. Menis, Ball, and Manning (39) have reported a method for the determination of mercuric ion in milligram or microgram quantities.

Gibson and White (26) have reported the use of triphenylmethylarsonium chloride as an indicator in the titration of ferrous ions with 0.1 N $K_2Cr_2O_7$. At the end point

$((C_6H_5)_3CH_3As)_2Cr_2O_7$ is formed which imparts a yellow color to a layer of ethylene dichloride with which the solution is shaken. By this procedure ferrous ion can be titrated in the presence of such colored ions as Cu(II), Co(II), Ni(II), Cr(III), and Mn(II).

The only salt of tetratolylarsonium ion which has been reported is the iodide. This compound was prepared by Mann and Watson (36) by the Friedel-Crafts reaction. The starting materials were tri-p-tolylarsine and p-bromotoluene. Tarbell and Vaughan (69) prepared tri-p-tolylarsine from arsenic trichloride and p-tolylmagnesium bromide in 46% yield. Sachs and Kantorowicz (60) prepared tri-p-tolylarsine from p-tolylmagnesium bromide and arsenious acid, and Michaelis (41) prepared the compound from p-bromotoluene, arsenic trichloride, and sodium with ether as solvent. Carson and Wong (13) prepared tri-p-tolylarsine oxide from tri-p-tolylarsine and phenyl benzenethiolsulfinate but observed that on exposure to air the product became sticky and apparently recrystallized as needles to give the hydrate. They also observed that triphenylarsine oxide does not form a hydrate unless the oxide is boiled with water. No explanation was given as to why the tri-p-tolylarsine oxide forms a hydrate readily but the triphenylarsine oxide does not.

Tetraphenylphosphonium chloride or bromide has been prepared by Willard, Perkins, and Blicke (73), Gilman and Brown (27), Lyon and Mann (35), and Chatt and Mann (16).

In general the tetraphenylphosphonium salts are more water soluble than tetraphenylarsonium salts. Willard, Perkins, and Blicke (73) used tetraphenylphosphonium chloride for the gravimetric determination of perrhenate, permanganate, perchlorate, and cadmium as the chloride complex. Shinagawa, Matsuo, and Nezu (63) reported the amperometric titration of bismuth as the iodide complex with tetraphenylphosphonium chloride. Medoka and Eferova (38) used the reagent for the microtitration of zinc, cadmium, and permanganate and reported upon possible interferences.

Neeb (46), (47), (48), (49) has used tetraphenylphosphonium chloride in the determination of such platinum metals as iridium, palladium, platinum, and osmium.

The synthesis of triphenylselenonium chloride is described in Organic Syntheses by Leicester (34). Shinagawa, Matsuo, and Isshiki (61) have studied the polarographic behavior of triphenylselenonium chloride with bismuth. Very little use of the reagent has been made in analytical chemistry since the triphenylselenonium salts are somewhat more soluble than the triphenyltelluronium salts.

Triphenyltelluronium chloride was first prepared by Lederer (33). Matsuo and Shinagawa (37) investigated the polarographic behavior of the reagent and reported its use in the qualitative determination of several inorganic ions. However, the precipitates obtained with metal complex ions are too soluble to permit the direct use of the reagent in

quantitative analysis.

Triphenyltin chloride has been synthesized by Chambers and Scherer (15) and by Nad and Kocheshkov (44) (some abstractors spell it Nadj and Kozeschkow). Tri-p-tolyltin chloride has also been synthesized by Nad and Kocheshkov. Perhaps the most sensational work done with triaryltin compounds has been in the use of these compounds to determine fluoride ion. Ballczo and Schiffner (6) treated an aqueous solution containing fluoride ion at a pH from 4 to 9 with a saturated solution of triphenyltin chloride in chloroform. The two layers were stirred and then the aqueous and chloroform layers were poured through a filter. The precipitate was washed with a little water and a saturated solution of triphenyltin chloride in chloroform. The precipitate is obtained free of reagent, and interferences by phosphate, borate, ferric, aluminum, and zirconium ions are avoided. The accuracy is within 0.5%. Horton (30) claims that this procedure is the best method available at the present time for the determination of fluoride. Allen and Furman (3) have also developed a procedure for the determination of fluoride with triphenyltin chloride.

A few volumetric methods for the determination of fluoride have been developed but most of these methods are not accurate and are not specific for fluoride. Brandt and Duswalt (11) determined fluoride by a turbidimetric titration with calcium ion as titrant. They claimed that concentrations

of 0.01 to 0.09M fluoride ion could be determined with an average relative error of 2%. Thorium ion could also be used as the titrant to determine fluoride ion from 0.04 to 1.0 M with an average relative error of 2%. Interferences were observed from a large number of cations and anions but no interferences were observed from borate, chloride, bromide, acetate, nitrate, or zinc.

Powell and Menis (57) reported that macro and micro quantities of fluoride could be separated from inorganic materials by a pyrolytic method. The pyrolysis was carried out in a stream of moist oxygen in a fused silica reactor tube. The fluoride, which was volatilized, was absorbed in a small volume of dilute sodium hydroxide, and then determined by either an acidimetric or spectrophotometric titration.

Simons, Wagner, and Muller (65) prepared tetra-p-tolylgermanium and tri-p-tolylgermanium bromide. Brook and Mauris (12) prepared triphenylsilicon chloride (triphenylchlorosilane). Apparently the triarylgermanium and triarylsilicon chlorides are not stable in water but Steele and Kipping (67) readily prepared tri-p-tolylsilicol ($(C_7H_7)_3SiOH$).

Triphenyllead chloride has been prepared by Foster, Dix, and Gruntfest (25) by a slight modification of the method of Gilman and Robinson (28). Gilman and Robinson (28)

have also prepared tetraphenyllead. The lead compounds have not found extensive use as an analytical reagent, although Ford (24) used tetraphenyllead to form salt derivatives with some high molecular weight fatty acids.

Triphenylsulfonium chloride has been synthesized by Pitt (54). Shinagawa, Matsuo and Maki (62) reported the polarographic behavior of triphenylsulfonium chloride towards several metal ions. The reagent was used in the amperometric titration of mercury and bismuth halide complexes since the precipitates obtained with these complexes were insoluble.

More good derivatives are needed for identification of the low molecular weight aliphatic acids, sulfonic acids, and substituted aliphatic acids. The most common derivatives of organic acids are the amides, anilides, toluides, esters, and complex organic salts. Commonly the acid chloride is first prepared and subsequently it reacts with ammonia or the appropriate amine to form the amide or the N-substituted amide. The acid chloride of an organic acid is ordinarily prepared by the reaction of another acid chloride with the organic acid. Any acid chloride used to prepare an organic acid chloride will react with water in preference to the organic acid, which means the acid must be very nearly dry. It is generally not difficult to isolate and dry a solid acid; however, it is difficult to isolate and dry some liquid acids, especially the low molecular weight water soluble acids. This difficulty is especially true when it becomes

necessary to identify an ester of a low molecular weight liquid acid. The ester is usually saponified with a strong base. The mixture is then acidified with a mineral acid and the organic acid is steam distilled from the mixture. In such cases it would be desirable to make the derivatives from aqueous solutions.

Reid (58) was able to prepare the p-nitrobenzyl esters from the sodium salts of organic acids. However, the melting points of many of the esters of the low molecular weight aliphatic acids are too low for convenient use. Also, most of the derivatives had to be prepared in alcoholic solution. The phenacyl esters and the para halogenated phenacyl esters were also investigated by Hann, Reid, and Jamieson (29). Drake and Sweeny (21) prepared a series of p-phenylphenacyl esters and at present are probably the best organic derivatives that can be made in the presence of water. However, many of the melting points of the derivatives mentioned above are too close together, lower than desired, and the procedures for preparing the esters are long and tedious.

Attempts have been made to use salts as organic acid derivatives. Ambler and Wherry (4) prepared salts of some napthalenesulfonic acids using amines. These salts have no definite melting points. Chambers and Scherer (14) and later Donleavy (20) reported the preparation of S-benzylthiouronium salts which give sharp melting points. However, the melting

points of the homologous series are too close together. Also, hydrolysis of the salts readily occurs so Donleavy (20) suggests the use of non-aqueous solvents since benzyl mercaptan produced in the hydrolysis reactions possesses a disagreeable odor. Dewey and coworkers (18), (19) prepared similar salts using S-p-bromobenzylthiouronium halidies as the reagents instead of S-benzylthiourea. The results were very much the same as those obtained by Chambers and Scherer (14). Pollard, Adelson, and Bain (53) prepared piperazonium salts by the action of piperazine hexahydrate on the acid, but the derivatives were water soluble and high concentrations of piperazine hexahydrate and the organic acid were required to obtain a precipitate. Stempel and Schaffel (68) prepared some phenylhydrazonium salts. Many halogen-substituted aliphatic acids such as alphabromopropionic, bromoacetic, and betabromopropionic acids merely split off hydrogen halide to yield a precipitate of the corresponding phenylhydrazine hydrohalide. Several acids, including crotonic, salicylic, and halogen-substituted benzoic acids, failed to precipitate. It is not certain whether the piperazonium and phenylhydrazonium salts can be prepared in aqueous solution. Ford (24) prepared some salt derivatives of the high molecular weight fatty acids. The salts prepared were those of triphenyllead, p-tolylmercuric, and phenylmercuric ions. Ford also prepared other derivatives of some high molecular weight fatty acids. The following derivatives of lauric, myristic, palmitic, and stearic

acids were prepared: (1) N-acylcarbazoles, (2) N-acylphenothiazines, (3) N-acyl-p-toluenesulfonamides, (4) p-phenylphenacyl esters, (5) p-nitroanilides, (6) N-acylsaccharins, (7) 2,4-dinitrophenylhydrazides, (8) N-acyl-2-nitro-p-toluidines, (9) p-tolylmercuric salts, (10) phenylmercuric salts, (11) triphenyllead salts, (12) monoureides, (13) monothioureides, (14) p-xenylamides, (15) p-diphenyl ketones, (16) 2,8 diacyl carbazole, (17) p-acylaminobenzoic acids, and (18) diacylbenzidines. The derivatives of 1,2,3,5,8 and 14 were prepared by heating the acid chlorides with the appropriate compound to 100-160 degrees without a solvent. Derivatives of 4 were prepared from p-phenylphenacyl bromide and the sodium salts. Derivatives of 6 were prepared by refluxing the Na salt of saccharin and the acid chlorides in dry chloroform. Derivatives of 7 were prepared by refluxing the base and the chloride in dry benzene. Derivatives of 9,10, and 11 were prepared by refluxing diphenylmercury, di-p-tolylmercury, and tetraphenyllead with the acids in xylene. Derivatives of 12 and 13 were prepared by refluxing the acids with urea or thiourea in anhydrous pyridine. Derivatives of 15 and 16 were prepared by the Friedel-Crafts reaction in dry carbon disulfide and dry nitrobenzene, respectively. Derivatives of 17 and 18 were prepared by refluxing acid chlorides in anhydrous pyridine with p-aminobenzoic acid and benzidine, respectively, with two equivalents of acid chloride in the latter case.

In summarizing, one may say that if water is present in an organic acid the preparation of an amide is impractical. The esters have some merit as derivatives which can be prepared in water, but in many cases the melting points are too close together or too low to be desirable derivatives. Also, the procedures for preparing esters are long and tedious. Of the salt derivatives that have been prepared, those of phenylhydrazine and piperazine hexahydrate are the best as far as the melting points are concerned, but the authors report no use of water in the preparation of these salts.

The first tetraarylstibonium salts were prepared in 1940 when Chatt and Mann (16) prepared tetraphenylstibonium bromide and iodide by the Friedel-Crafts reaction. The starting materials were triphenylstibine and bromobenzene. Michaelis and Reese (42) were the first to prepare triphenylstibine, and Morgan and Vining (43) improved the technique. A method by which triphenylstibine is prepared by the reaction between antimony trichloride and phenylmagnesium bromide is given in Organic Syntheses, Collective Volume One, page 551. Willard, Perkins, and Blicke (73) prepared tetraphenylstibonium chloride and reported it to have a low solubility but used it for the determination of perchlorate and permanganate. Willard and Perkins (72) reported the use of tetraphenylstibonium chloride for the determination of permanganate, perrhenate, pertechnetate, perchlorate, periodate, fluoborate, and some complex metal chlorides. Potratz (55)

reported a method for the determination of fluoride by carbon tetrachloride solvent extraction from aqueous media. He states that tetraphenylstibonium sulfate has a high water solubility but the tetraphenylstibonium ion forms an insoluble precipitate with fluoride and offers the advantage over other fluoride precipitants in that it can be used in solutions containing sulfate, since tetraphenylstibonium sulfate is insoluble in carbon tetrachloride. Chloride and bromide ions are also extracted, but 99.2% of the fluoride can be recovered if the chloride ion is first removed by precipitation with excess silver ion.

Shinagawa, Matsuo, and Okashita (64) synthesized tetraphenylstibonium chloride and made a polarographic study of the reagent. A polarogram of the tetraphenylstibonium chloride solution showed a two-step wave with maxima at -0.8 and -1.2 volts vs. the saturated calomel electrode using 0.1 N KCl as the supporting electrolyte. The maxima were controlled by 0.01% Triton X-100 and the half-wave potentials were found to be -0.72 and -1.11 volts vs. the S. C. E. when the maxima suppressor was present. Bismuth and mercury were determined as the iodide complexes by amperometric titration with tetraphenylstibonium chloride at -0.85 volts vs. the S. C. E. The titration error was claimed to be not greater than 3%.

Affsprung and May (1) used tetraphenylstibonium sulfate as a qualitative reagent for organic acids. None of

the onium type compounds have been used for the determination of organic anions, and only a few of the cation complexes which could form a precipitate with onium type compounds have been reported. Affsprung and May (1) say that tetraphenylstibonium sulfate is of interest because of its high water solubility and relatively low solubility in organic solvents, such as carbon tetrachloride. These properties were advantageous in the use of tetraphenylstibonium sulfate as an analytical reagent. They prepared tetraphenylstibonium hydroxide and found equivalent weights of 450, 453, and 451 compared to the actual value of 447. Tetraphenylstibonium sulfate solution was prepared by dissolving a weighed amount of tetraphenylstibonium hydroxide in an exact volume of standard sulfuric acid and then diluting in a volumetric flask. The concentration was calculated from the weight of the hydroxide and the volume of the solution. They conclude that a new reagent has been found for the precipitation and subsequent identification of a number of organic acids. Some of the advantages of these derivatives are: (a) The derivatives are easily prepared and purified, (b) The derivatives are prepared from aqueous solution, whereas the majority of the known organic acid derivatives cannot be prepared from aqueous solution, (c) Of the salts prepared, the melting points are sufficiently far enough apart for identification, (d) Only very simple equipment is required, (e) The reactions are instantaneous, (f) The organic acid can be easily recovered

by dissolving the stibonium salt in water, making the solution basic, filtering off the tetraphenylstibonium hydroxide, and evaporating the solution to dryness. Two disadvantages are: (a) The reagent cannot be purchased at the present, although triphenylstibine dichloride can be, thus leaving one Grignard reaction to be performed, and (b) The closeness of the melting points of the acetate and propionate derivatives.

Considerable interest in organometallic compounds by a number of well-known chemists has been shown in the past. Horton (30) in a recent book has issued challenges for future investigation. For example, better methods are needed for the determination of fluoride ion. Fluoride is most commonly determined as CaF_2 or as PbFCl, and the precipitates are gelatinous, difficult to filter, and easily form colloids. Triphenyltin chloride has been used for the gravimetric determination of fluoride. The precipitate has a good gravimetric factor, filters well and washes easily. Horton (30) says that all present quantitative methods for fluoride depend on: (a) Precipitation of an insoluble fluoride which is weighed, (b) Excess metal ion estimated by gravimetric methods, (c) Volumetric, or (d) Colorimetric methods. Many difficulties are involved in precipitation of inorganic fluorides since numerous other anions also form insoluble salts with the same metal ion. No future is seen for the discovery of more selectively precipitated inorganic fluoride salts, but investigation

of other organometallic compounds might lead to the discovery of a still more desirable precipitant than triphenyltin chloride.

OBJECTIVES

The objectives of this research were:

1. To synthesize a new organic onium-type compound which will qualitatively identify organic acids. The derivatives formed by the reagent should be stable, have sharp melting points, and be easy to recrystallize. The melting points should be far enough apart so that the derivatives can be easily distinguished.
2. To investigate the polarographic behavior of the onium-type compound and develop a polarographic method for the equivalent weight determinations of the derivatives. Polarography would be especially suitable for the determination of the percent tetra-p-tolylstibonium of the tetra-p-tolylstibonium organic acid derivatives, since only small amounts of material are needed in polarographic analyses.
3. To examine the solubility characteristics of the various derivatives and find which derivatives were extremely insoluble. The tetra-p-tolylstibonium ion would be useful for the quantitative determination of those organic anions with which it formed extremely insoluble precipitates.

4. To consider other onium-type compounds with different properties so that comparisons could be made as to which onium-type compound was most suitable for a particular analysis.

APPARATUS

All melting points were taken in capillaries using the melting point apparatus in Figure 1 unless otherwise stated.

The apparatus was filled with silicone oil. The oil was heated by means of a resistance wire coil in conjunction with a powerstat, and stirred by means of an electric stirrer. The stirring served a twofold purpose. First, it gave a uniform temperature between the stirrer and the wire coil, thus removing the temperature differential that might be in the liquid in that area. Second,it circulated the oil in a counter-clockwise motion. Using a good powerstat with this apparatus, it was not difficult to fix the rate of temperature rise at 0.5 degree per minute or lower when desired.

Potentiometric titrations were made with a Beckman Zeromatic pH meter.

The solubilities of the tetratolylstibonium salts were determined using the thermostated water bath shown in Figure 2.

The water was stirred vigorously by means of a large electrically powered stirrer. Two thermometers were

used to adjust the thermostat control box to the proper setting. One of the thermometers was calibrated in hundredths of a degree. The water in the bath was heated by an electric heater and cooled by means of a coil through which cool water could be circulated. At twenty degrees this apparatus kept the temperature at 20 $\pm$ 0.1 degrees. A micro set thermoregulator was used.

Current-voltage curves were obtained by means of the Sargent Model XXI Recording Polarograph shown in Figure 2. An H-cell was used to make the polarograms with a saturated calomel electrode in one-half of the cell. The other half of the cell was used to hold the solution to be analyzed. The S. C. E. half cell was separated from the solution to be analyzed by a porous sintered-glass disk. A diagram of the cell is shown in Figure 2.

REAGENTS USED

Eastman Kodak - white label grade

- Formic acid
- Acetic acid
- Propionic acid
- n-Butyric acid
- Isobutyric acid
- n-Valeric acid
- Isovaleric acid
- alpha-Bromopropionic acid
- beta-Bromopropionic acid
- m-Hydroxybenzoic acid
- p-Hydroxybenzoic acid
- m-Iodobenzoic acid
- p-Iodobenzoic acid
- m-Nitrobenzenesulfonic acid
- o-Bromobenzoic acid
- m-Bromobenzoic acid
- p-Bromobenzoic acid
- Dichloroacetic acid
- o-Chlorobenzoic acid
- m-Chlorobenzoic acid
- p-Chlorobenzoic acid
- o-Toluic acid
- m-Toluic acid
- p-Toluic acid
- p-Toluenesulfonic acid
- alpha-Chloropropionic acid
- beta-Chloropropionic acid
- Furoic acid (2-Furoic)
- Sodium 5-nitro-6-chloro-Toluene-3-sulfonate

Eastman Kodak - yellow label

- Fumaric acid

Matheson Co. - reagent grade

- m-Nitrobenzoic acid

Mallinckrodt - analytical reagent

Chloroacetic acid	Oxalic acid
Potassium fluoride	Sodium bromide

Merck - reagent grade

Sulfosalicylic acid

J. T. Baker Co. - analyzed reagent

Trichloroacetic acid

Eimer and Amend Co. - reagent grade

Dichloroacetic acid

Baker and Adams - A. C. S. reagent

Sodium chloride

Fisher Scientific Co. - certified reagent

Potassium nitrate

Coleman and Bell Co. - reagent

Potassium Biphthalate

FIGURE 1

Melting Point Apparatus

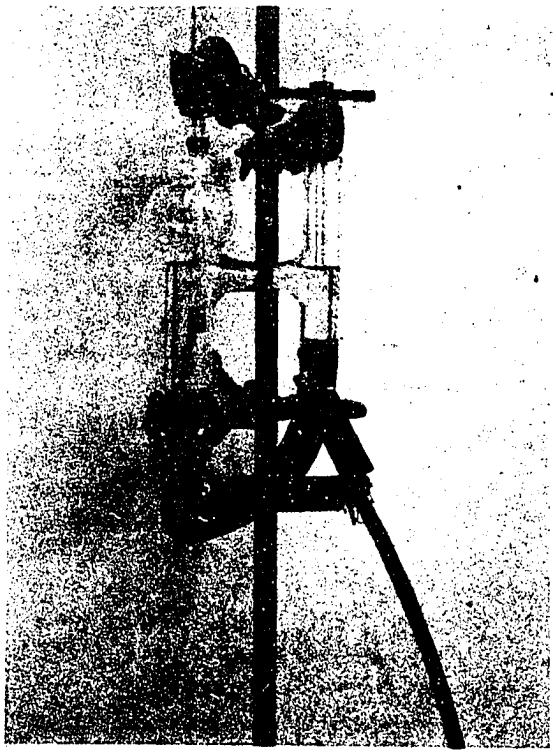
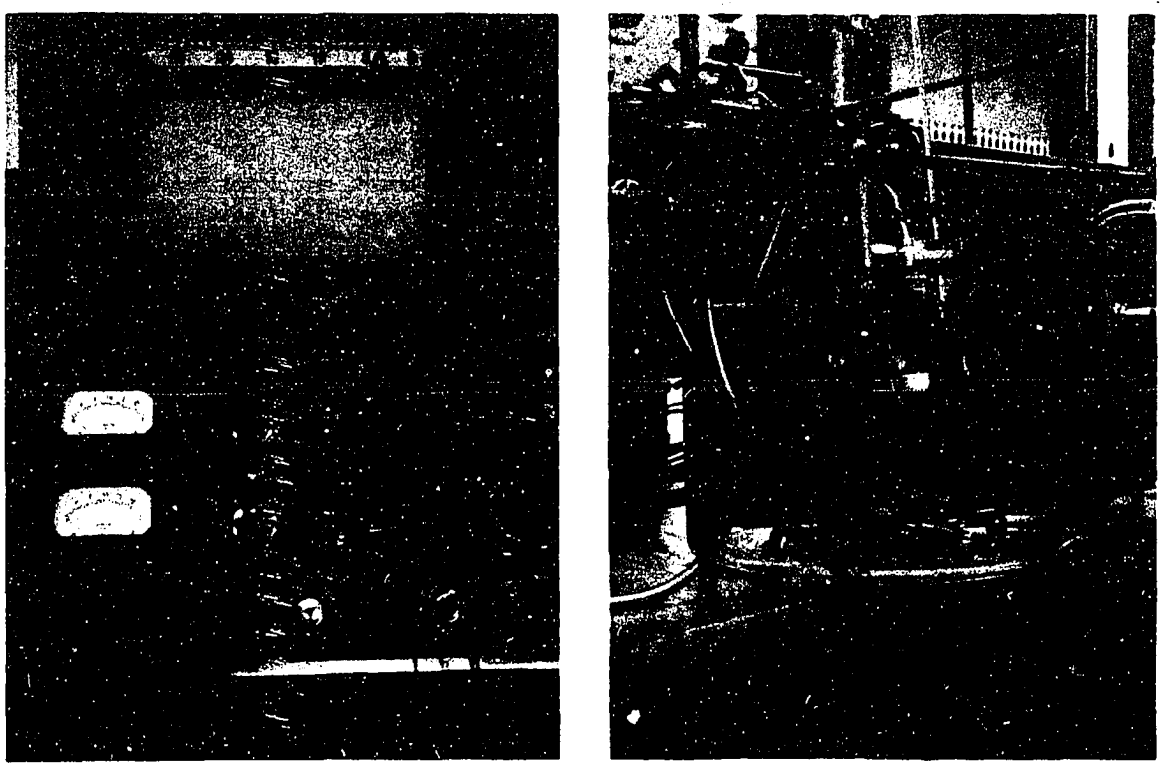


FIGURE 2

The Polarographic Assembly, Made Up of a Tank of Nitrogen, H-Cell, Thermostated Water Bath, and Sargent Model XXI Polarograph.



CHAPTER II

EXPERIMENTAL

Preparation of p-Bromotertiarybutylbenzene

A mixture of 98 grams (0.73 mole) of t-butylbenzene and 1 gram of iodine was placed in a flask with stirrer and reflux condenser and 120 grams (0.75 mole) of bromine was added dropwise. The reaction was cooled with icewater. The reaction between the t-butylbenzene and the bromine proceeds vigorously and HBr fumes are given off. After all of the bromine was added, the reaction mixture was heated on a steam bath and then with an electric heater to remove bromine vapors. The oily product was washed with dilute sodium carbonate until the oil became a light yellow in color, and then was washed twice with distilled water. The oil was dried overnight over anhydrous calcium chloride, filtered, and distilled. The fraction distilling from 229-233 degrees was kept. Yield was 106 grams (68% yield).

Preparation of Tri-p-tertiarybutylbenzenestibine Dichloride

A Grignard reagent was prepared by dropping 106

grams (0.52 mole) of p-bromotertiarybutylbenzene dissolved in 250 ml. ether into a flask containing 11.4 grams (0.47 mole) of magnesium in 75 ml. of dry ether. The reaction was initiated by grinding the magnesium with a stirring rod. After the reaction had subsided, 25 grams (0.109 mole) of antimony trichloride dissolved in 250 ml. of ether was added dropwise and a tan precipitate which gradually darkened was formed. After all of the antimony trichloride had been added, the mixture was refluxed on a steam bath for 4 hours. The reaction mixture was decomposed by pouring the mixture into 100 ml. of cold 1:10 hydrochloric acid. The aqueous layer was separated and extracted with two 100 ml. portions of ether. The combined ether extracts were evaporated on a steam bath and the viscous oil was dissolved in 250 ml. of carbon tetrachloride and oxidized with chlorine gas. No attempt was made to cool the reaction mixture which became hot during the reaction but in future preparations an attempt should be made to keep the reaction mixture cool to prevent side reactions from occurring. The reaction mixture changed colors from a cream to an orange to a light brown during the oxidation and became a dark brown when the volume of the solution was evaporated to 100 ml. A precipitate formed on cooling and turned white when washed with a little carbon tetrachloride. The compound was recrystallized from benzene-ether. Yield of

pure tri-p-tertiarybutylbenzenestibine dichloride was 25.1 grams (37%). It is believed that the yield could be increased if the carbon tetrachloride solution is kept cool at all times. It is suggested that the carbon tetrachloride solvent be removed by a stream of air when concentrating the solution. The melting point of the recrystallized product was 308-309 degrees. The calculated percentages of carbon and hydrogen in the compound are 60.83% and 6.64%, respectively. The percentages of carbon and hydrogen found by experiment were 60.59% and 6.80%, respectively.

Preparation of Tetra-p-tertiarybutylbenzenestibonium Sulfate

During the effort to develop a reagent which would form extremely insoluble precipitates with the organic acids, the synthesis of tetra-p-tertiarybutylbenzenestibonium sulfate was attempted. This reagent would have a molecular weight of 1405 compared to a molecular weight of 956 for tetraphenylstibonium sulfate, and therefore could be expected to form more insoluble precipitates with the organic acids.

Tri-p-tertiarybutylbenzenestibine dichloride is very insoluble in ether so that it is difficult to perform the last reaction step in which the compound is reacted with excess Grignard reagent. 23.6 grams of tri-p-tertiarybutylbenzenestibine dichloride was finally dissolved in 120 ml. benzene, 300 ml. tetrahydrofuran, and 250 ml. ether, and this

mixture was reacted with an excess of the Grignard reagent of p-bromotertiarybutylbenzene. The reaction mixture was refluxed for 4 hours and allowed to stand for 1½ days. The reaction mixture was decomposed in 500 ml. of cold 1:20 sulfuric acid. The aqueous lsyer was separated and extracted with two 100 ml. portions of ether and the combined ether extracts evaporated until an oil remained. The oil was extracted with two 125 ml. portions of hot dilute (1:20) sulfuric acid but no precipitate was obtained when the extracts were made basic with ammonium hydroxide. The tetra-p-tertiarybutylbenzene-stibonium sulfate was so insoluble in water that a soluble salt could not be found and as a consequence the compound could not be used as an organic reagent.

Preparation of Tribiphenylstibine Dichloride

Activated magnesium was prepared by adding 5 ml. of dry ether dropwise to a well-stirred mixture of 5 grams 30-80 mesh Mg powder, 100 ml. of dry benzene, and 2.5 grams of iodine. When the color of the iodine had completely disappeared, the solvent was distilled with the aid of an oil bath, the solid residue being maintained at 150-160 degrees for about 10 minutes. The activated Mg was transferred to a dry rubber-stoppered bottle. Reactivation before use is recommended and may be effected by heating in a test tube until gas evolution ceases and the color of iodine appears. About 0.2 gram of activator was sufficient to initiate a reaction.

A Grignard reagent was prepared by refluxing 2.5 grams of activated Mg, 19 grams of p-bromobiphenyl, and 40 ml. dry ether for 12 hours. The p-biphenylmagnesium bromide (0.0815 mole) was reacted with 5.24 grams (0.023 mole) of antimony trichloride in 150 ml. ether for 5 hours under reflux. The reaction mixture was decomposed in distilled water and a white flocculent precipitate was formed. The precipitate was extracted with HCl to remove any $Sb(OH)_3$ present and the undissolved precipitate was removed by filtration. The residue was dissolved in carbon tetrachloride and chlorinated with Cl_2. Some crystals formed and the solvent was removed on a steam bath. The dark residue was dissolved in benzene and reprecipitated with alcohol. A yellowish white flocculent precipitate formed and was removed by filtration. The precipitate was dried and yellowish white crystals formed which melted at 136-143 degrees.

An unsuccessful attempt was made to prepare tetrabiphenylstibonium sulfate but there was very little reaction between tribiphenylstibine dichloride and p-biphenylmagnesium bromide. Tribiphenylstibine dichloride is only slightly soluble in benzene and is almost completely insoluble in ether so that the last step of the synthesis of tetrabiphenylstibonium sulfate is difficult to perform. Also, p-bromobiphenyl is so unreactive that it is difficult to form the Grignard reagent.

Preparation of p-Bromotoluene

p-Bromotoluene was prepared by a slight modification of the method described in Organic Syntheses, Collective Volume 1, p. 136. A mixture of 63 grams (0.25 mole) of copper sulfate pentahydrate, 20 grams (0.31 gram atom) of copper turnings, 114 grams (1.1 moles) sodium bromide, 30 grams (16.3 cc, 0.28 mole) of concentrated sulfuric acid, and one liter of water was refluxed over a flame for 3 to 4 hours until the color became yellowish.

When the hydrobromic acid-cuprous bromide solution was prepared, a solution of 107 grams (1 mole) of p-toluidine and 196 grams (107 cc, 1.9 moles) of concentrated sulfuric acid in one liter of water was cooled below 20 degrees and diazotized with a solution of 70 grams (1 mole) of sodium nitrite in 125 cc of water. The sodium nitrite solution was added in small portions with stirring. The mixture was allowed to stand for 30 minutes while the temperature was maintained between 15 and 20 degrees by means of an ice bath.

A 5 liter round-bottomed flask containing the hydrobromic acid-cuprous bromide solution was arranged for steam distillation. After the copper solution was heated to boiling, the diazonium solution was gradually added from a separatory funnel and a vigorous current of steam was passed through the reaction mixture at the same time. This procedure required about 2 hours.

The aqueous distillate was made alkaline with sodium hydroxide solution and the p-bromotoluene was separated from the water layer. The crude product was washed once with concentrated sulfuric acid, and then with water. The product was dried over calcium chloride or anhydrous sodium sulfate, filtered, and distilled. The yield of pure product was about 110 grams (about 60% yield) and was distilled at 183-185 degrees.

Preparation of Tetra-p-tolylstibonium Sulfate

Tetra-p-tolylstibonium salts have not been reported upon and salts of the tetra-p-tolylstibonium ion must be prepared. To prepare tetra-p-tolylstibonium sulfate 343 grams of p-bromotoluene was dissolved in 900 ml. of ether and added dropwise to 48.64 grams of magnesium in 400 ml. of ether. After the resulting Grignard reagent was prepared 114.1 grams antimony trichloride was dissolved in 400 ml. ether and added slowly with stirring over a 40 minute period. Two hundred ml. of ether was added and the mixture was refluxed and stirred for a period of 1½ hours. The mixture was allowed to stand overnight and the addition compound was decomposed with 1 liter of cold water and 40 ml. of hydrochloric acid. The aqueous layer was separated and washed with two 200 ml. portions of ether. The ether was evaporated on a steam bath and the residue was repeatedly extracted with carbon tetrachloride. The tri-p-tolylstibine was

oxidized in the carbon tetrachloride solution with chlorine. A gummy residue which floated was removed and the carbon tetrachloride was evaporated with a stream of air. The carbon tetrachloride solution must be cooled during the oxidation and evaporation to prevent side reactions from occurring. The tri-p-tolylstibine dichloride was recrystallized from benzene-hexane mixtures. The melting point was 156.0-157.5 degrees. The yield was 154 grams, or 66% based on the antimony trichloride. One hundred and thirty-six grams (0.29 mole) of tri-p-tolylstibine dichloride was dissolved in 220 ml. benzene and 950 ml. ether. This solution was added to a solution of a Grignard reagent prepared from 21.6 grams of magnesium and 152 grams p-bromotoluene in 600 ml. of ether. The mixture was stirred and refluxed for 4 hours and allowed to stand for 3 days. The addition compound was decomposed with 1:10 sulfuric acid. The aqueous portion was separated and extracted with three 100 ml. portions of ether. The organic layer was evaporated to 200 ml. and extracted 3 times with hot dilute (1:75) sulfuric acid. The extracts were combined and excess ammonium carbonate was added. A voluminous precipitate, apparently the carbonate, appeared. This was filtered and washed with water. The precipitate was then dissolved in dilute sulfuric acid, treated with Norite and filtered. The hydroxide of tetra-p-tolylstibonium ion was then precipitated by the slow addition of 0.2N ammonium hydroxide. The first gummy particles of precipitate were

removed and discarded. Very pure tetra-p-tolylstibonium hydroxide could be obtained if the precipitation was carried out slowly and carefully with stirring. The particles of precipitate which formed as the precipitation with ammonium hydroxide was continued were continually removed and discarded until a very white, powdery precipitate was obtained. The hydroxide was washed with water and dried in a vacuum desiccator for 1½ days. The equivalent weight of the hydroxide was determined by dissolving a known amount in an excess of standard sulfuric acid and back-titrating with standard sodium hydroxide. A pH meter was used to determine the equivalence point. The equivalent weight was found to be 507, as compared to the theoretical value of 503. Methyl red was shown to be a suitable indicator for the titration. A list of the antimony compounds prepared, along with their melting points and carbon-hydrogen analyses is shown in Table 1.

Preparation of Tetra-p-tolylstibonium Derivatives

All of the derivatives of the tetra-p-tolylstibonium ion obtained from organic acids were prepared in a similar manner. About 20-30 ml. of a solution of the salt of the organic acid were adjusted to a pH slightly less than 7 with dilute ammonium hydroxide and sulfuric acid, and treated with 8-10 ml. of 0.05 M tetra-p-tolylstibonium sulfate. A precipitate usually formed immediately. If a precipitate did not appear at room temperature, it appeared when the solution

was cooled in an ice bath. In each case the precipitate was filtered and washed with a little cold water. In the case of the acetate, formate, propionate, and some of the sulfonic acids, 25 ml. of 0.2 N acid was treated with dilute ammonium hydroxide until a pH of 5.8-6.2 was reached. Fifteen milliliters of the reagent, approximately 0.05 molar, was added and the volume reduced to 25-30 ml. with a stream of clean air. Diamond-shaped crystals were formed whose melting points were sharp and which did not change after recrystallization of the salt from n-hexane. The acetate, formate, and propionate derivatives were recrystallized from n-hexane by dissolving the derivative in the hot solvent and allowing the solution to cool to room temperature. Derivatives other than the low molecular weight aliphatic acids can be recrystallized from benzene-hexane or from ethyl alcohol and water. Usually better looking, more crystalline derivatives with sharper melting points can be obtained by recrystallization from benzene-hexane. The derivative salts were dissolved in the minimum amount of benzene, filtered, and treated with n-hexane until the solution became cloudy. The solution was heated until the cloudiness disappeared and then chilled in an ice bath or in a refrigerator. The derivative salts were filtered on paper with suction and allowed to dry at a temperature of about 60 degrees, and the melting points were taken in capillaries. Each salt was recrystallized until a

constant melting point was obtained. Usually two recrystallizations were adequate. Each salt was prepared independently at least two times. The heating rate of the bath averaged 0.5 degrees C. per minute at the melting point. A list of the derivatives and their melting points are shown in Table 2.

Although tetra-p-tolylstibonium sulfate is quite soluble in water, the reagent is insoluble in hexane and if a derivative is to be recrystallized from hexane or from benzene and hexane, then filtering is recommended as soon as the derivative is dissolved in hot hexane or benzene and before the solution is allowed to cool.

Some difficulty was encountered in the preparation of the derivatives when the organic acids were not pure. Some of the halogen-substituted organic acids were impure and purification of the organic acids was required before sharp melting derivatives could be obtained. The liquid acids and some of the solid acids were distilled to achieve purification unless the boiling points were so high that decomposition occurred. Most of the solid water-insoluble aromatic acids were recrystallized from sulfuric acid and ammonium hydroxide. Some of the acids were recrystallized from ethanol and water.

The solubilities of the tetratolylstibonium salts of formic, acetic, propionic, and benzoic acids were determined. In each case a concentrated solution of the salt was

TABLE 1

The Melting Points and Analyses of Some Organic Antimony Compounds

Organic Sb Compound	Melting Point	Theory % C	Theory % H	Found* % C	Found* % H
Tri-p-tolylstibine	125.0-126.0				
Tri-p-tolylstibine dichloride	155.5-157.0	54.07	4.52	53.87 54.09	4.58 4.53
Tetra-p-tolylstibonium chloride**	227.0-228.5	64.46	5.41	64.21	5.50
Tri-p-tertiarybutyl-benzenestibine dichloride**	308.0-309.0***	60.83	6.64	60.59	6.80
Tri-p-biphenyl-stibine dichloride**	163.0-166.0				
Tetra-p-tertiarybutyl-benzenestibonium chloride	varied	69.61	7.60	66.61	7.71

* Analyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

** New Compounds

*** Taken on melting point block

TABLE 2

Melting Points of Some Tetra-p-tolylstibonium Organic Acid Salts

Salt	Melting Point
Formate	110.5-111.0
Acetate	157.0-158.1
Propionate	119.1-120.6
n-Butyrate	127.7-129.0
Isobutyrate	123.5-125.0
n-Valerate	107.0-108.7
Isovalerate	125.0-126.5
Chloroacetate	120.8-122.0
Dichloroacetate	153.5-154.9
Trichloroacetate	209.5-211.0
beta-Bromo Propionate	217.5-219.0
beta-Chloro Propionate	225.5-227.0
alpha-Chloro Propionate	136.5-138.3
alpha-Bromo Propionate	130.0-131.0
Lactate	137.2-139.2
Furoate	167.0-168.5
Hydrogen Mesaconate	194.0-195.8
Hydrogen Maleate	162.8-164.0
Picrate	128.5-130.0
Hydrogen Fumarate	223.5-224.0

TABLE 2
(Continued)

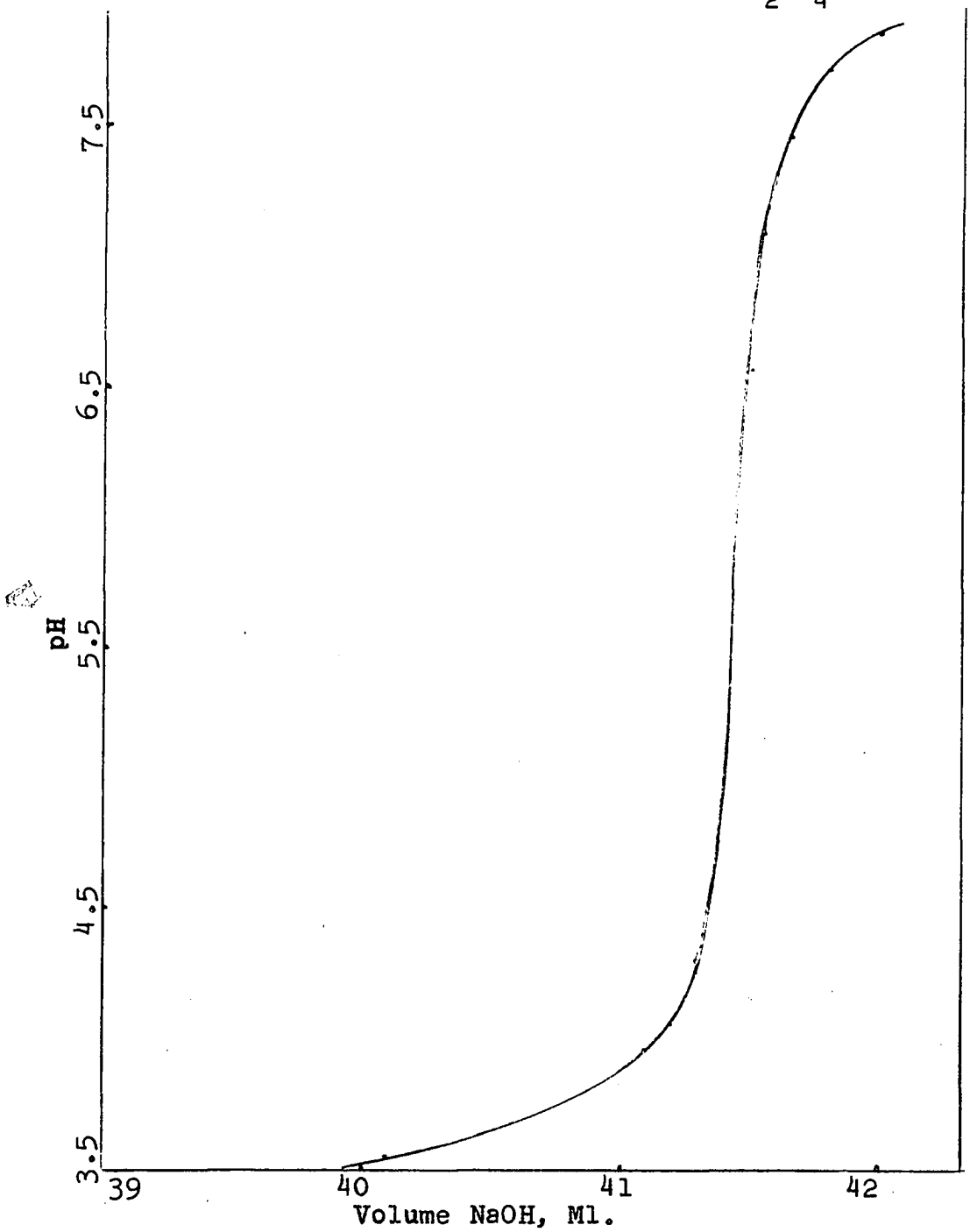
Salt	Melting Point
Hydrogen Oxalate	235.0-236.1
Hydrogen phthalate	177.7-178.8
2,5 Dichloro Benzene Sulfonate	151.8-153.0
Sulfosalicylate	143.0-145.0
p-Toluene Sulfonate	159.0-160.0
m-Nitrobenzene Sulfonate	132.7-134.0
Benzene Sulfonate	167.0-168.5
5-Nitro-6-Chloro-Toluene-3-Sulfonate	139.0-141.0
Salicylate	193.6-195.0
o-Toluate	129.5-131.0
m-Toluate	180.5-182.0
p-Toluate	191.8-193.3
Acetyl Salicylate	193.0-194.3
m-Hydroxy Benzoate	182.5-184.0
p-Hydroxy Benzoate	218.0-219.5
o-Bromo Benzoate	194.5-196.0
m-Bromo Benzoate	178.0-179.8
p-Bromo Benzoate	150.5-152.0
3,4,5, Trimethoxy Benzoate	189.5-191.0
Anisate	191.0-192.7
o-Chloro Benzoate	195.2-196.7

TABLE 2
(Continued)

Salt	Melting Point
m-Chloro Benzoate	181.5-183.0
p-Chloro Benzoate	172.2-174.0
m-Iodo Benzoate	165.2-167.0
p-Iodo Benzoate	232.0-233.0
m-Nitro Benzoate	192.5-193.5
o-Methoxy Cinnamate	154.0-156.0
m-Methoxy Cinnamate	151.5-152.8
p-Methoxy Cinnamate	178.6-180.2
Benzoate	169.5-171.1
Perchlorate	214.5-216.0
Hydroxide	90 (initial)
Chloride	227.0-228.5
Bromide	228.5-230.0
Fluoride	153.5-155.4
Nitrate	172.0-173.0

FIGURE 3

Plot of Ml. 0.1251 N NaOH vs. pH in the Equivalent Weight Determination of 0.8859 gm. Tetra-p-tolylstibonium Hydroxide Dissolved in 50.00 Ml. of 0.1282 N H_2SO_4.



prepared in hot water and then cooled and thermostated at 20.0 ± 0.1 degrees overnight. Aliquots were taken and evaporated, at temperatures not exceeding 60 degrees C., until all excess water was removed. Finally the residues were dried to constant weight in a vacuum desiccator and the solubilities calculated. A few samples were then placed in an oven at 110 to 115 degrees C. for several hours with no further loss in weight being observed in any case, indicating that no simple hydrates were formed and that the desiccator drying was adequate. A list of the solubilities of some tetra-p-tolylstibonium salts, along with their melting points and carbon-hydrogen analyses, are shown in Table 3.

Polarographic Behavior of Tetra-p-tolylstibonium Compounds

As can be seen from the survey of previous work on onium-type compounds, considerable success has been achieved in the use of these compounds in polarography and amperometric titrations.

As a brief introduction we may say that voltammetry is an electrochemical type of analysis which depends upon the relation between the current in amperes flowing through the electrolysis cell and the potential in volts across the cell. Voltammetry with a dropping-mercury electrode is generally called polarography, and the instruments employed are called polarographs.

Some advantages of the dropping-mercury electrode

TABLE 3

Solubilities and Analyses of Some Tetra-p-tolylstibonium Derivatives

Tetra-p-tolylstibonium Salt	Theory		Found*		Solubility g. Salt per 100 g. Water at 20.0 ± 0.1 Deg. C.
	% C	% H	% C	% H	
Formate	65.56	5.50	65.74	5.51	1.29, 1.35
Acetate	66.08	5.73	66.24	5.92	0.46, 0.34
Propionate	66.57	5.95	66.60	5.74	0.392, 0.386
Chloride	64.46	5.41	64.21	5.50	
Benzene Sulfonate	63.47	5.17	63.62	4.96	

* Analyses by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

are: (a) Hydrogen has a very high overvoltage on a mercury surface, which means that it is possible to exceed the decomposition potentials of many active metals which could not be studied at a platinum cathode. (b) The metal surface continually renews itself and therefore cannot become fouled or poisoned.

The mathematical theory of the polarograph has been worked out and the equation resulting from the theory is known as the Ilkovic equation: I_d equals $607\ nD^{1/2}\ Cm^{2/3}\ t^{1/6}$ where I_d is the average current in microamperes during the life of the drop, n is the number of faradays of electricity required per mole of the electrode reaction, D is the diffusion current of the reducible or oxidizable substance in the units cm^2/sec, C is the concentration in millimoles per liter, m is the rate of flow of mercury from the dropping electrode capillary expressed in the units mg/sec, and t is the drop time in seconds and is usually measured at the half-wave potential. The temperature is not mentioned in the Ilkovic equation, but each term is temperature-dependent to some extent, and D is a function of the temperature. The diffusion current I_d increases at the rate of 1 or 2 % per degree in the vicinity of room temperature. The temperature of the electrolysis cell should therefore be controlled to at least $\pm$ 0.5 degrees.

Many factors which are difficult to handle in a

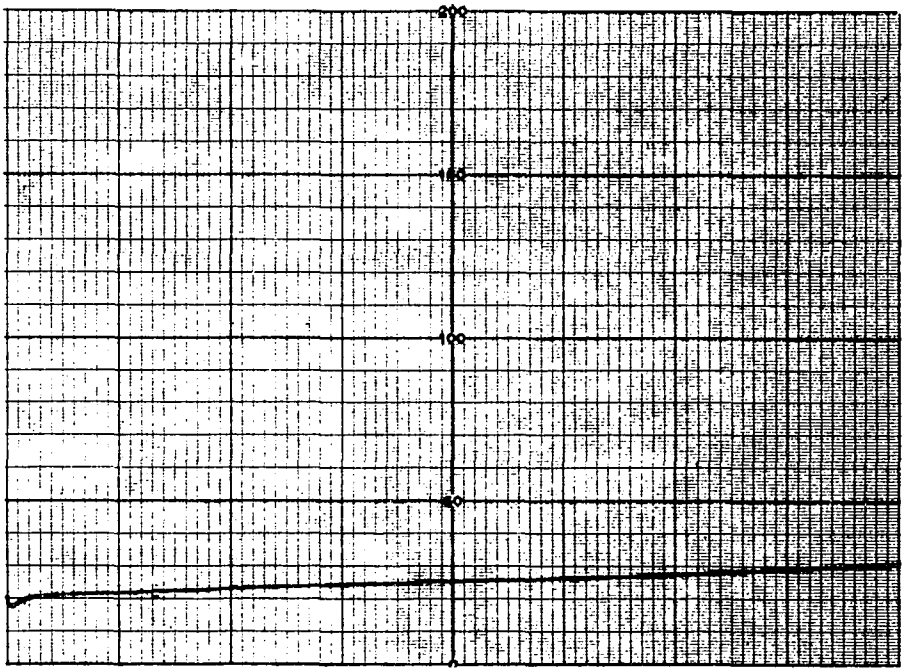
polarographic analysis may be avoided by making only relative measurements. To do this it is necessary to prepare a standard solution of the desired ion and determine its current-voltage curve under the same conditions as the unknown. Then the Ilkovic equation can be applied in the simplified form I_d equals KC. The proportionality constant can be evaluated graphically and need not be resolved into its theoretical equivalent.

Ions can be identified by their half-wave potentials. The half-wave potential $E_{\frac{1}{2}}$ is determined by the intersection of the curve by a horizontal line drawn midway between the two horizontal portions of a current-voltage curve. The value of $E_{\frac{1}{2}}$ is characteristic of a particular ion in a particular supporting electrolyte. The value of $E_{\frac{1}{2}}$ has no relation to the quantitative determination of the metal.

The limiting current is the sum of three components: the residual current, the migration current, and the diffusion current. The residual current is the small current which will flow even in the absence of a reducible ion. The residual current curve shown in Figure 4 is typical. The migration current is due to the reduction of reducible ions, such as the tetra-p-tolylstibonium ions, which are attracted to the cathode by electrostatic forces and is eliminated in practical work by the addition of a relatively high concentration of a supporting electrolyte such as potassium sulfate whose

FIGURE 4

Residual Current Curve of 0.1 N K_2SO_4 Supporting Electrolyte Made Up 0.01% in Triton X-100.



ions are neither reduced or oxidized at the microelectrode within the potential range being studied.

A. Polarogram of the supporting electrolyte.

The Sargent Model XXI Polarograph was used to obtain all polarograms. The Sargent Model XXI was set at 2 volts on SPAN, 0 volts on INITIAL, 3 volts span on DC EMF, the INITIAL EMF was set at OFF, the DAMPING was set at 1, the DME at minus, and UPSCALE and DOWNSCALE at 0. The first polarogram was the residual current curve shown in Figure 4. A potassium sulfate solution 0.1 N in potassium ion was made 0.01% Triton X-100. The solution was deaerated with a stream of nitrogen for 15 minutes and the current-voltage curve was obtained with the saturated calomel electrode. A diagram of the assembly used to obtain polarograms is shown in Figure 2.

B. Polarograms of tetra-p-tolylstibonium sulfate.

A 5×10^{-4}M tetra-p-tolylstibonium sulfate solution containing a supporting electrolyte of potassium sulfate which was 0.1M in potassium ion was deaerated with nitrogen and current-voltage curves were obtained with the S. C. E. as reference electrode. A two-stepped reduction wave was obtained with the first half-wave potential at -0.66 V and the second half-wave potential occurred at -1.11 V. The first wave had a maximum, which was suppressed by making the solution 0.01% in Triton X-100. Maxima occurring with

stibonium concentrations of 1 to 2 x 10^{-4} M can be suppressed by making the solution 0.005% in Triton X-100, but are observed for higher stibonium concentrations unless the Triton X-100 concentration is raised to 0.01%. The current-voltage curve of tetra-p-tolylstibonium sulfate is shown in Figure 5.

C. Relation between the half-wave potential of tetra-p-tolylstibonium sulfate and pH.

As can be seen in Figure 6 the half-wave potential of the first wave remained constant at -0.66 volts vs. the S. C. E. at pH values between 2 and 6, whereas the half-wave potential of the second wave shifted to more negative potentials with increasing pH. A Beckman Zeromatic pH meter with a glass-calomel electrode assembly was used for the determination of the pH values of the standard tetra-p-tolylstibonium sulfate solution. An attempt was made to use $KHSO_4$ as supporting electrolyte instead of potassium sulfate, but in the relatively strong acid solutions a large hydrogen wave developed at a potential of about -0.9 volts vs. the S. C. E. and interfered with the determination of the height of the first wave of the tetra-p-tolylstibonium sulfate. The solution became turbid at pH values above 6.5 unless very pure tetra-p-tolylstibonium hydroxide was used in preparing the standard solutions. If pure hydroxide is used, the solutions do not become turbid until the pH exceeds 7. As can be seen from Figure 3, tetra-p-tolylstibonium ion forms the insoluble hydroxide when the pH exceeds 7.

FIGURE 5

Current-Voltage Curve for 5 x 10^{-4} M Tetra-p-Tolyl-stibonium Sulfate Made up 0.1 N in K^+ as K_2SO_4 and 0.01% in Triton X-100 and Adjusted to a pH of 3.7.

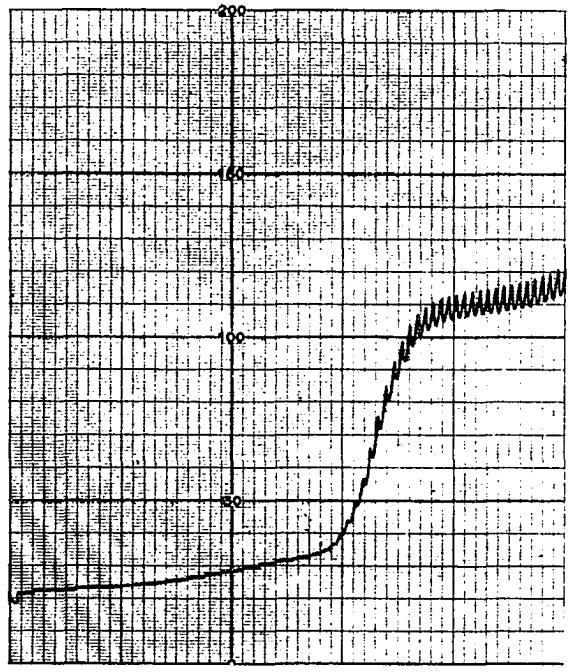
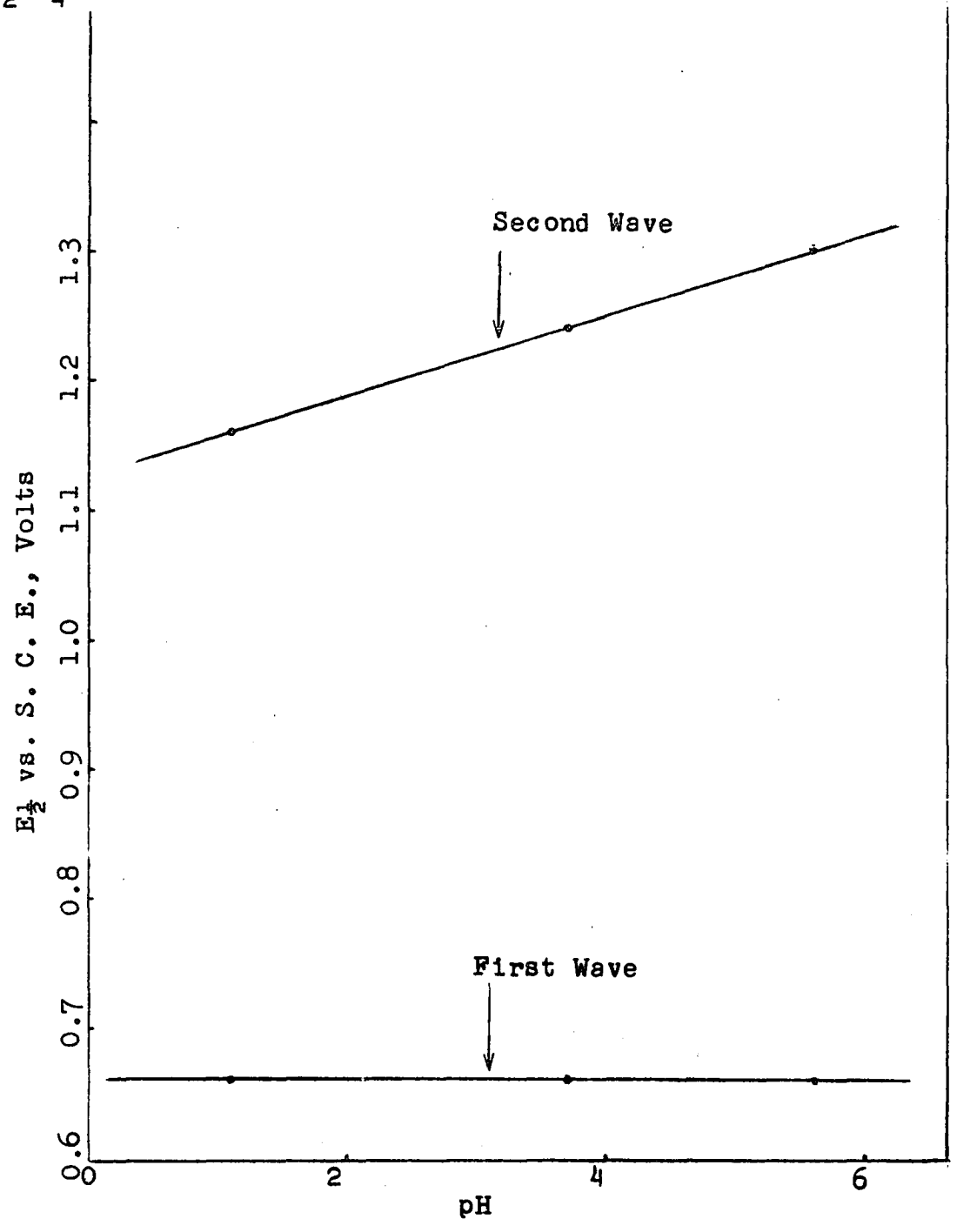


FIGURE 6

Plot of Half-wave Potential vs. pH for 5×10^{-4} M Tetra-p-tolylstibonium Sulfate. Solution is 0.1 N in K^+ as K_2SO_4 and 0.01% in Triton X-100.



D. The dependence of wave-heights on the concentrations of tetra-p-tolylstibonium sulfate.

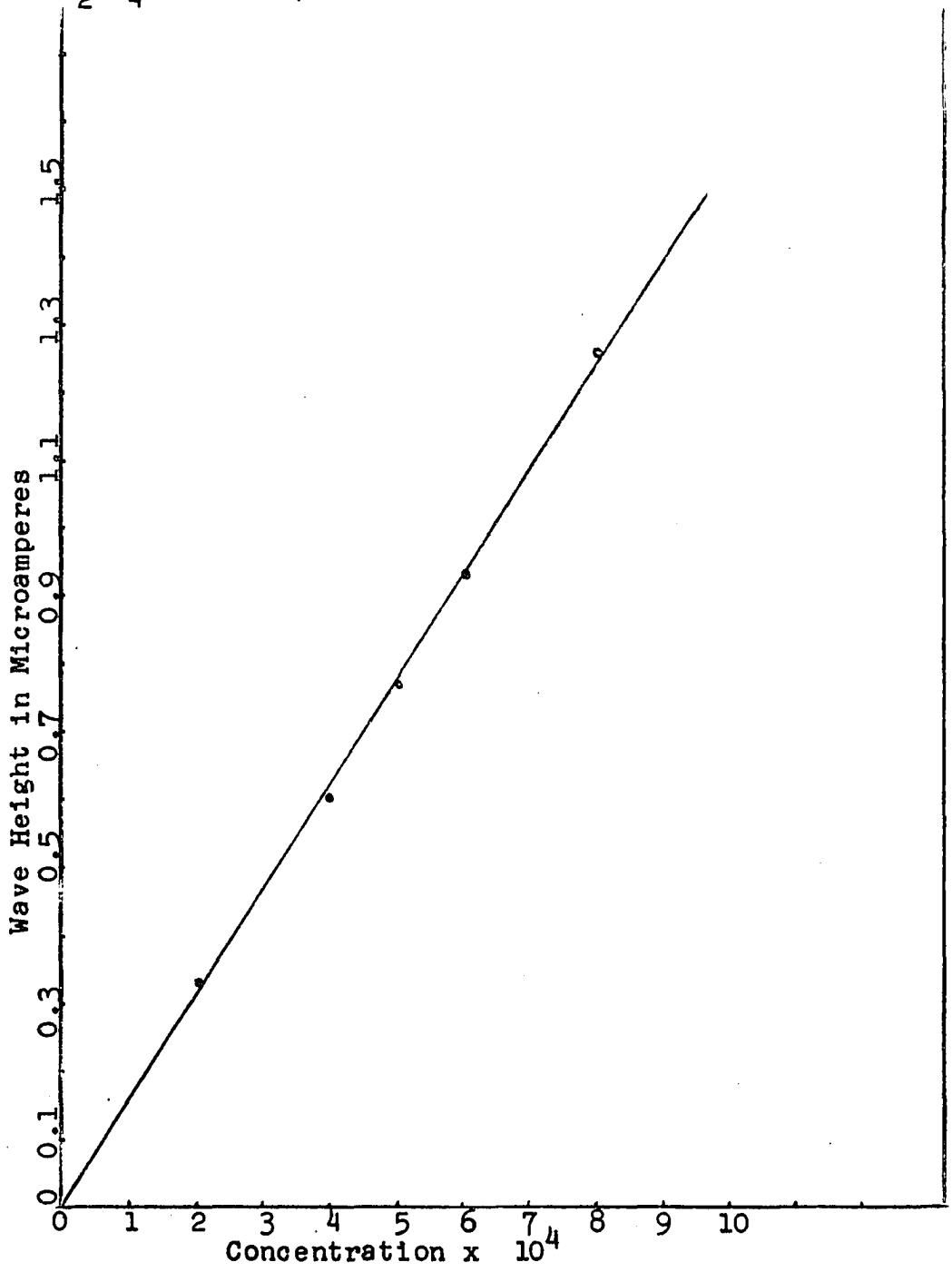
The polarograms of tetra-p-tolylstibonium sulfate solutions were obtained at concentrations between 1.0×10^{-4} to 1.0×10^{-3} M. A plot of wave height vs. concentration was made for a series of standard solutions and a straight line was obtained for the first wave. The plot for the second wave did not show a linear relation. The plot for the first wave is shown in Figure 7. Since the wave height is proportional to the concentration for the first wave, it is possible to use polarography for the quantitative determination of tetra-p-tolylstibonium ion or its salts.

E. The relation between the wave height of tetra-p-tolylstibonium sulfate and the height of the mercury column.

Because the diffusion current is proportional to the quantity $m^{2/3}t^{1/6}$, any variations of m or t will cause corresponding changes of the diffusion current. Numerous authors have shown that $m^{2/3}t^{1/6}$ (and therefore the diffusion current) is proportional to the square root of the effective pressure of mercury. This is the basis of a simple and frequently used method of ascertaining whether the height of a wave is diffusion-controlled: if $I_d/h_{eff.}^{\frac{1}{2}}$ is not constant within experimental error over a wide range of mercury pressures, the current must be partially or wholly governed

FIGURE 7

Plot of Wave Height vs. Concentration for Tetra-p-tolylstibonium Sulfate Solutions Made 0.1 N in K^+ as K_2SO_4 and 0.01% in Triton X-100.



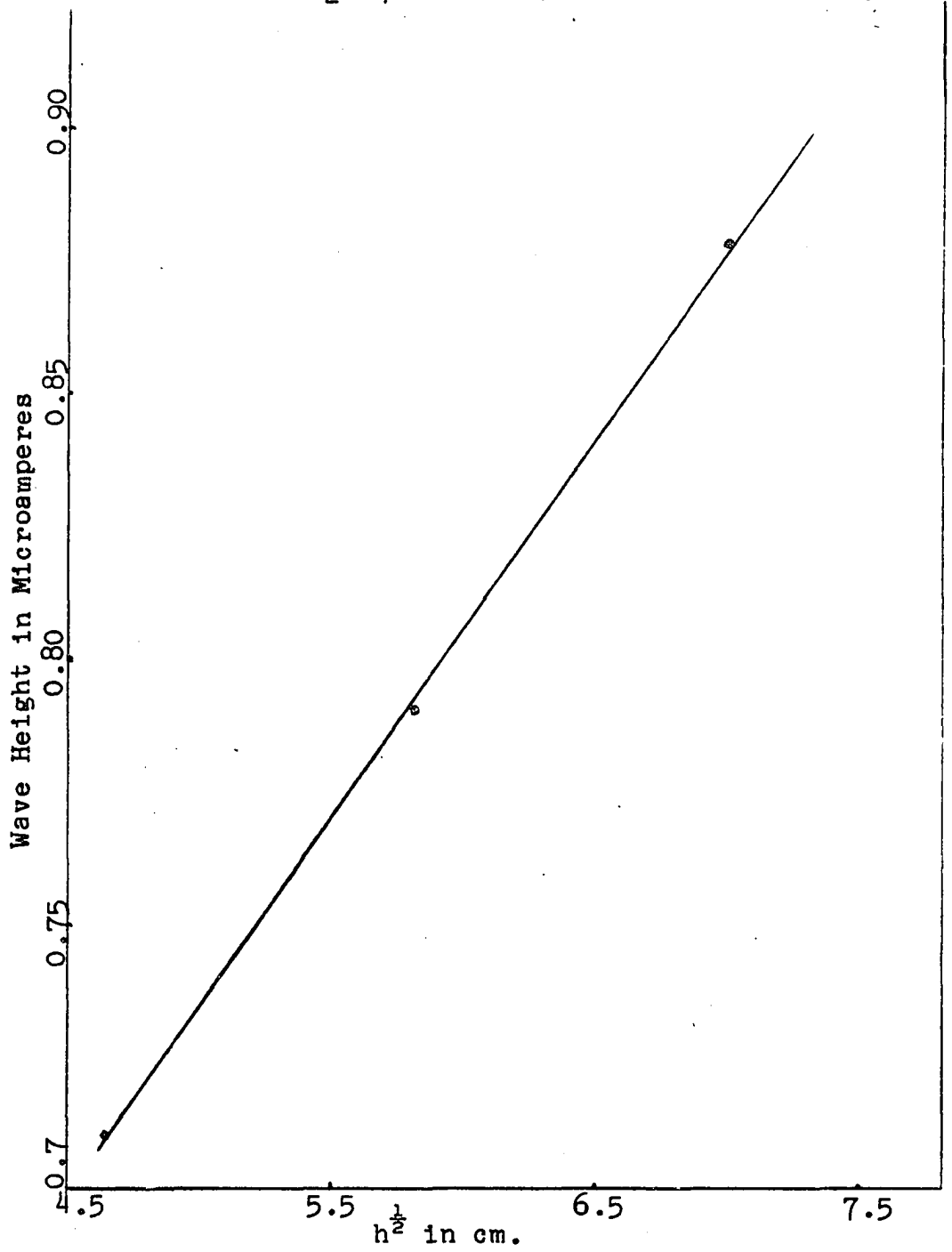
by the rate of some process other than diffusion to the electrode surface. A solution was made 5 x 10^{-4} M in tetra-p-tolylstibonium sulfate, 0.1 M in K^+ as K_2SO_4, 0.01% in Triton X-100, and adjusted to pH 3.7 with dilute ammonium hydroxide and sulfuric acid. The solution was deaerated with nitrogen as usual, and polarograms were obtained at a number of different mercury column heights. A plot of the square root of the heights of the mercury column vs. the corresponding diffusion currents at those heights yielded a straight line. The data are shown in Figure 8. This experiment demonstrates that the current is diffusion-controlled.

F. Analysis of tetra-p-tolylstibonium organic acid salts by polarography.

Although the melting points listed for the various organic acid derivatives serve as a good method of identification, an analysis of a given derivative would be highly desirable. A simple method for the determination of the percent tetra-p-tolylstibonium of a number of derivatives was developed. Standard tetra-p-tolylstibonium sulfate solutions of concentrations of 2,4,5,6, and 8 x 10^{-4} M were made 0.1 M in K^+ as K_2SO_4 and adjusted to pH's between 3.5 and 4.0 by means of sulfuric acid and ammonium hydroxide. The tetra-p-tolylstibonium organic acid derivatives were carefully weighed on an analytical balance, dissolved in the minimum amount of sulfuric acid, made 0.1 M in K^+ as K_2SO_4, and

FIGURE 8

Plot of Wave Height vs. the Square Root of the Height of Mercury Column for 5×10^{-4} M Tetra-p-tolylstibonium Sulfate Made 0.1 N in K^+ as K_2SO_4 and 0.01% in Triton X-100. pH=3.7.



also adjusted to pH's between 3.5 and 4.0 with sulfuric acid and ammonium hydroxide. Polarograms of the standard solutions and the tetratolylstibonium organic acid solutions were made, and the wave heights of the first waves were determined. A standard curve was made by plotting the wave heights vs. the concentrations of the different standard solutions. The concentrations of the tetratolylstibonium organic acid solutions were determined from their positions on the standard curve. The concentrations of the tetratolylstibonium organic acid solutions determined by polarography are compared with the concentrations determined from the weight of the organic acid derivative in solution, and the results are shown in Table 4.

Solubility Characteristics of the Organic Salts of Tetra-p-tolylstibonium Ion

In general the organic salts are soluble in chloroform, acetone, alcohol, and benzene. The aliphatic acid derivatives are more easily soluble in hexane than are the aromatic acid derivatives.

The best method found, in general, for the recrystallization of an unknown organic acid derivative was to dissolve the salt in the minimum amount of benzene, filter, add hexane until the solution became cloudy, warm the solution until the cloudiness disappeared, and then cover the solution and cool. Usually beautiful diamond-shaped crystals formed whose melting points did not change when recrystallized a second time. A few of the acid derivatives formed needle

TABLE 4

Polarographic Analysis of Some Tetra-p-tolyl Derivatives by Polarography

Derivative	% Tetra-p-tolylstibonium			% Carbon		
	Theory	Found		Theory	Found	
		Run 1	Run 2		Run 1	Run 2
Formate	91.53	90.41	90.24	65.56	64.76	64.64
Acetate	89.17	91.85	88.20	66.08	68.07	65.36
Propionate	86.94	85.03	86.27	66.57	65.11	66.06
Benzene Sulfonate	75.57	75.57	75.80	63.47	63.47	63.66
p-Toluene Sulfonate	73.97	75.15	71.00	63.94	64.96	61.37
Butyrate	84.81	88.20	85.69	67.03	69.71	67.73
Isobutyrate	84.81	84.00	82.41	67.03	66.39	65.13
Valerate	82.79	82.79	82.79	67.48	67.48	67.48
Isovalerate	82.79	84.78	85.20	67.48	69.10	69.44
Chloroacetate	83.87	83.54	84.65	62.15	61.91	62.73
2-Furoate	81.41	78.76	80.65	66.35	64.19	65.73

TABLE 4
(Continued)

Derivative	%Tetra-p-tolylstibonium			% Carbon		
	Theory	Found		Theory	Found	
		Run 1	Run 2		Run 1	Run 2
Hydrogen Mesaconate	79.02	78.50	79.68	64.41	63.99	64.95
Lactate	84.52	83.00	82.10	64.71	63.55	62.86
Alphachloropropionic	81.89	80.42	82.47	62.70	61.57	63.25
Alphabromopropionic	76.19	75.21	78.62	58.34	57.59	60.20
Betabromopropionic	76.19	75.58	78.34	58.34	57.87	59.99
Hydrogen Phthalate	74.65	74.35	75.00	66.38	66.11	66.69
Hydrogen Maleate	80.87	80.22	80.22	63.91	63.40	63.40
o-Toluic	78.25	74.89	78.54	69.58	66.59	69.84
m-Toluic	78.25	77.12	78.28	69.58	68.58	69.61
p-Toluic	78.25	75.91	77.10	69.58	67.50	68.56
Benzoate	80.06	81.18	81.18	69.21	70.18	70.18

like crystals and some of the derivatives formed leaflets. Some of the low molecular weight aliphatic acid derivatives were so soluble in benzene and in hexane that it was usually best to dissolve such a derivative in the minimum amount of hexane, filter, remove some of the solvent with a stream of air until the solution became cloudy, warm the solution until the cloudiness disappeared, and then cover the solution and chill. The acetate, formate, and propionate derivatives were recrystallized in this manner. Better results were usually obtained when the benzene and hexane solutions were filtered to remove any impurities present which were not soluble in benzene or hexane.

Water was a poor recrystallizing solvent for the organic salts when used alone. The large majority of the salts were too insoluble in water to permit its use as a recrystallizing solvent. Most of the organic salts were too soluble in alcohol to permit its use as a recrystallizing solvent. A combination of alcohol and water was used successfully in the purification of some of the derivatives, but quite often the derivatives formed were powdery or slightly oily. In all cases, the organic acid derivatives could either be recrystallized from benzene and hexane, hexane, or from alcohol and water. No organic or inorganic acid derivative has been prepared which cannot be recrystallized from at least one of the solvent combinations mentioned above.

If the derivative did not recrystallize well from benzene and hexane, the solvents were removed by a stream of air or by a combination of heat and a stream of air. The residue was then recrystallized from hexane and if the recrystallization was unsatisfactory, the hexane was removed by a stream of air and the residue would be recrystallized from alcohol and water. Best results in the use of alcohol and water as a recrystallizing solvent combination were obtained when as little water was used as possible.

The organic acids salts are too soluble in acetone to make it useful as a recrystallizing solvent. (A little work has been done with the use of carbon tetrachloride or cyclohexane as recrystallizing solvents but these compounds offer no advantage over the solvents used).

The Determination of the Water Solubilities of Some Organic Salts of Tetra-p-tolylstibonium Ion

The water solubilities of tetra-p-tolylstibonium formate, acetate, propionate, fluoride, and benzoate were determined. Each solubility was determined according to the following general procedure: An excess of the pure salt was added to about 10 ml. of distilled water in a 25 ml. Erlenmeyer flask. The mixture was heated 30-40 degrees above room temperature with shaking. The sample was permitted to stand several hours at temperatures above 25 degrees. In each case there was solid tetra-p-tolylstibonium salt in equilibrium

with the solution. The flask was then placed in a thermostated water bath which had been previously adjusted to 20.0 ± 0.1 degrees. See Figure 2. The salt solution was placed in the thermostated bath for 3 to 5 hours and was frequently shaken. A piece of filter paper was wrapped tightly around the end of a clean pipette and kept in place with a rubber band. While the solution remained in the bath a sample of the salt solution was pipetted through the filter paper and transferred to a weighed 25 ml. Erlenmeyer flask. The sample was weighed and the water was evaporated slowly by means of heat and a stream of clean air. When nearly dry, it was removed from the heat and evaporated to dryness in a vacuum desiccator. The solubility was calculated on the basis of grams of salt in 100 grams of water. A sample of tetra-p-tolylstibonium acetate was heated in an oven at 105 degrees for 3 hours after drying in a vacuum desiccator, and the additional weight loss was 0.25 mg. per 100 mg. of salt. The small loss of weight shows that no hydrate of tetra-p-tolylstibonium acetate was formed.

Preparation of Tri-p-tolylarsine

Sixty-five grams (2.83 gram atoms) of small chunks of sodium was placed in a 2 liter, 3 necked, round-bottomed flask and covered with 450 ml. of benzene made 2% in ethyl acetate. The benzene-ethyl acetate mixture was stirred with the sodium for at least 30 minutes in order to activate the

sodium. The flask was fitted with a condenser, mechanical stirrer, and a 500 ml. dropping funnel containing a mixture of 85 grams (0.47 mole) of arsenic trichloride and 153.1 grams (1.21 moles) of p-chlorotoluene. About 15 ml. of the arsenic trichloride and p-chlorotoluene mixture was dropped into the flask, and the reaction mixture was heated and stirred on a steam bath until it darkened and boiled spontaneously. The remainder of the arsenic trichloride and p-chlorotoluene mixture was added dropwise, with stirring and heating, over a period of 1-1.5 hours at such a rate that gentle boiling was maintained. When the addition was complete, the mixture was stirred and heated under reflux on a steam bath for 4 hours and allowed to stand overnight.

The next day the hot reaction mixture was filtered through a large Buchner funnel into a 2 liter flask. The residue was washed with two 100 ml. portions of hot benzene, and then transferred to a 1 liter beaker, boiled with 300 ml. of benzene, and filtered, the same funnel and flask being used. This extraction process was repeated 3 times.

The combined benzene filtrates were placed in a beaker and evaporated until a thermometer placed in the liquid registered 230 degrees C. The residue solidified on cooling to a crystalline mass, and was almost pure tri-p-tolylarsine. The tri-p-tolylarsine was recrystallized by dissolving the compound in the minimum amount of benzene and adding

an equal volume of ethyl alcohol. The mixture was allowed to stand in a refrigerator overnight. Small light-yellow diamond-shaped crystals formed which melted at 147.0-148.5 degrees. Seventy grams of crystals were obtained. The filtrate was concentrated by boiling and a second crop of crystals was obtained. Total yield was 82 grams, or 59% yield based on the p-chlorotoluene.

An attempt was made to prepare tri-p-tolylarsine by substituting toluene for benzene as solvent with no ethyl acetate. An attempt was also made to prepare tri-p-tolylarsine by using benzene as solvent with no ethyl acetate present. Very poor yields were obtained in the last two cases, indicating that the presence of ethyl acetate is essential to activate the sodium metal and allow the reaction to go to completion. In order to obtain better yields, it is also suggested that the combined benzene filtrates be evaporated from an open beaker until the temperature of the liquid reaches 230 degrees rather than distill the mixture at a lower temperature under reduced pressure, since some tri-p-tolylarsine may be distilled under reduced pressure if the temperature is not carefully controlled.

The residue from the benzene extractions should be treated with ethanol to destroy the unreacted sodium before being discarded.

Preparation of Tri-p-tolylarsine Oxide

A 2 liter, 3 necked, round-bottomed flask was equipped with a stirrer, thermometer, and a 60 ml. dropping funnel. 71.5 grams (0.205 mole) of tri-p-tolylarsine dissolved in about 1 liter of acetone was added to the flask. Tri-p-tolylarsine is quite insoluble in cold acetone and care must be taken to prevent reprecipitation when the solution is cooled. Twenty-nine grams (0.255 mole) of 30% hydrogen peroxide was added dropwise with stirring over a period of 30 minutes. Any tri-p-tolylarsine which was precipitated when the acetone solution was cooled to room temperature dissolved as the hydrogen peroxide was added. Therefore, it may be possible to use less acetone in future preparations. Care must be taken to prevent the reaction mixture from becoming too hot when the hydrogen peroxide is added. When the addition of hydrogen peroxide was complete, stirring was continued for 30 minutes, and the acetone was removed by distillation.

The flask containing the residual yellow oil was fitted with a water trap and condenser, and 125 ml. of benzene was added. The water was then removed by azeotropic distillation. This process was repeated twice. The flask containing the tri-p-tolylarsine oxide was stoppered and allowed to stand for 2 hours, and when the flask was shaken the oil quickly crystallized to a white solid.

Preparation of Tetra-p-tolylarsonium Chloride

The tri-p-tolylarsine oxide was dissolved in 1400 ml. of hot benzene. Care was taken to prevent contact of the tri-p-tolylarsine oxide with the air. To this solution was added dropwise with stirring a solution of p-tolylmagnesium bromide which was prepared from 8.26 grams (0.34 mole) magnesium, 52.8 grams (0.309 mole) p-bromotoluene, and 250 ml. dry ether. A brown viscous solid separated and care was taken that the Grignard solution was not added too fast to prevent the solid from forming a large viscous ball. The mixture was stirred for 15 minutes and then stirred and refluxed for 1 hour. The heating was discontinued when the viscous precipitate became more waxy and very difficult to stir. The solution was allowed to stand for 3 hours and the brown precipitate became considerably more viscous and waxy. The mixture was stirred and refluxed for 30 minutes but this procedure was discontinued when the precipitate became extremely waxy. The mixture was filtered hot through a Buchner funnel. It was observed that the filtrate became cloudy on the surface when exposed to the air, possibly indicating that not all of the Grignard reagent had been used up. The precipitate was washed with two 100 ml. portions of benzene and then heated and stirred with about 500 ml. water. A flocculent white precipitate formed which dissolved when treated with a little concentrated HCl, and formed a red-brown oil. A total of 250 ml. of concentrated HCl was added

to the solution and the mixture was stirred and placed in the refrigerator overnight. A small amount of benzene was removed the next day with a separatory funnel and the solution again placed in the refrigerator. No crystals formed and the acid was removed and the oil dissolved in chloroform. The solution was filtered and the chloroform was removed by evaporation. Concentrated HCl was again added to the oil and the mixture was allowed to stand for a few days. A few needles formed, but not enough of the material was obtained to allow extensive investigation of the material. A few needles were also formed when the oil was extracted with boiling water and the water treated with solid sodium chloride until the solution became saturated.

A list of the arsenic compounds prepared and their melting points is shown in Table 5.

Preparation of Tellurium Tetrachloride

Fifty grams of tellurium (0.392 mole) was placed in a dry 250 ml. flask fitted with a sidearm containing a number of ampoules. A slow stream of chlorine was introduced into the flask and heat was applied to the flask to initiate the reaction between the elements. After the reaction had started, heat was no longer necessary in the early stages of the reaction. The presence of tellurium (II) chloride is indicated by the murky black liquid that first forms. As soon as an excess of chlorine had been added to complete the

TABLE 5

Melting Points of Some Organic Arsenic and Tellurium Compounds

Compound	Melting Point
*Tri-p-cumylarsine	140.8-142.8
*Tri-p-cumylarsine oxide (may be tri-p-cumylarsine dihydroxide)	168-169(decomposes)
Tri-p-tolylarsine	147.0-148.5
Tri-p-tolylarsine oxide	
Tri-p-tolylarsine dihydroxide	
Diphenyltellurium dichloride	163-166
Triphenyltelluronium iodide	248.2-249.5
Tetra-p-tolylarsonium iodide	253-255

* New Compounds

conversion of the tellurium to tellurium (IV) chloride, the liquid changed to dark-red color and became clear. A yellow vapor was produced by heating the red liquid. This condensed as a yellowish-white crystalline material on the cool part of the sidearm and gradually filled the ampoules. By careful heating the tellurium (IV) chloride was distilled into the ampoules and the ampoules were sealed off with an oxygen torch. The slow stream of chlorine was continued throughout the distillation and sealing operations. With care in distillation fairly good yields were obtained.

Tellurium tetrachloride was also prepared by another method. 25.5 grams of tellurium metal was ground to a powder in a mortar and treated with 100 ml. of sulfur chloride (practical) with stirring. The reaction was stirred for 6-8 hours and the excess sulfur chloride was poured off. The crude tellurium tetrachloride was recovered by extraction of the impurities with carbon disulfide. The yellowish-green precipitate was dissolved in ether and filtered to remove any tellurium metal present. The ether was removed by an oil vacuum pump. Yield of crude tellurium (IV) chloride was about 45 grams (84% yield).

Preparation of Triphenyltelluronium Iodide

A solution of phenylmagnesium bromide was prepared from the reaction of 30 grams of bromobenzene and 4.6 grams of magnesium in 150 ml. ether. The reaction mixture was

refluxed for 1 hour, then cooled in an ice bath and 10 grams of tellurium tetrachloride dissolved in 150 ml. of ether was added rapidly with stirring. A black precipitate was formed immediately. The reaction mixture was decomposed in 100 ml. of cold 1:10 hydrochloric acid. The black solid was separated from the ether and water layers by filtation, washed with cold ether, and extracted with hot 95% ethanol. The solvent was evaporated on a steam bath and the residual solid obtained was extracted with boiling water and filtered. A solution of potassium iodide was added to the filtrate and a yellowish-orange precipitate formed upon cooling. The precipitate was recrystallized from water and a small yield of yellowish-white needles was obtained. The needles melted at 248.2-249.5 degrees C., which corresponds to the melting point of triphenyltelluronium iodide as reported by Lederer (33).

An attempt was made to convert the triphenyltelluronium iodide to the chloride by boiling the triphenyltelluronium iodide with silver chloride for 1 hour. The precipitates turned lime green. When the filtrate from the reaction was evaporated very few crystals were obtained. Some of the original triphenyltelluronium bromide-chloride solution was used to make qualitative tests with various anion solutions. Precipitates were obtained with periodate, permanganate, dichromate, iodide, $SnCl_4^{-2}$, and $HgCl_4^{-2}$. No precipitates were obtained with acetate, propionate, and several other solutions

of organic anions.

Very poor yields were obtained for the synthesis of triphenyltelluronium chloride by the method discussed above, so an alternative method of preparation was sought. Although very little work has been reported on triaryltelluronium and triarylselenonium compounds, it appears that these compounds are quite similar in nature. Leicester (34) reported the preparation of triphenylselenonium chloride from selenium tetrachloride was too complex in all cases, and proposed that triphenylselenonium chloride be prepared from diphenylselenonium dichloride. An attempt was made to prepare diphenyltelluronium dichloride by a method similar to that used by Leicester to prepare diphenylselenonium dichloride.

Preparation of Diphenyltellurium

One hundred and eighty grams of powdered potassium hydroxide (3.205 moles) and 194 grams (1.52 moles) of powdered tellurium were thoroughly mixed and heated on an oil bath to 140 degrees, at which temperature they fused together to form a purple mass. An ice cold solution of diazotized aniline hydrochloride prepared from 69 grams (0.74 mole) of aniline was added slowly and in small portions at a time to a solution of the fused mass in 400 ml. of ice water. To complete the reaction, the solution was separated from the viscous tellurium-containing black mass in the bottom of the reaction vessel and heated to boiling. While still hot this

was poured back through the viscous black mass, which was then stirred with the liquid. The precipitate of tellurium was filtered off, and the lower liquid layer of the filtrate containing the diphenyltellurium separated. The tellurium was washed with ether and the washings combined with the diphenyl telluride. The combined liquids were placed in a flask connected to a water aspirator and heated to 120 degrees in an oil bath. A red oil remained.

Preparation of Diphenyltellurium Dichloride

The red oil was dissolved in an excess of concentrated nitric acid and treated with concentrated hydrochloric acid. A large amount of gas was evolved and no precipitate was obtained. This method was used in the preparation of diphenylselenium dichloride from diphenylselenium, but evidently is not applicable in the preparation of diphenyltellurium dichloride from diphenyltellurium. Rheinboldt and Petragnani (59) suggested that diphenyltellurium dichloride be prepared by the chlorination of diphenyltellurium.

Phenylmagnesium bromide was prepared from 14.6 grams of magnesium and 94.2 grams (0.6 mole) of bromobenzene in 200 ml. ether. The reagent was diluted with 300 ml. of dry benzene and added dropwise (within 30 minutes) to an ice water cooled and vigorously stirred solution of 27.0 grams (0.1 mole) of tellurium tetrachloride in 300 ml. ether and the reaction mixture was refluxed and stirred for 2 hours. The

reaction mixture was decomposed in a cold dilute ammonium chloride solution. The aqueous layer was separated from the organic layer by means of a separatory funnel and the organic layer was washed 3 times with 50 ml. portions of distilled water. The organic layer was dried over anhydrous magnesium sulfate and evaporated by low heat to a small volume. The remainder of the organic solvent was removed with an oil vacuum pump. The red-orange oil was dissolved in 100 ml. of carbon tetrachloride and treated with chlorine gas until the color of the solution turned dark green. A white precipitate formed when some of the solvent was evaporated and petroleum ether was added to complete the precipitation. Some of the precipitate was recrystallized with benzene-petroleum ether. The melting point was 163-166 degrees, and the yield was 10.5 grams (about 30% yield). Rheinboldt and Petragnani (59) reported a melting point of 162-163 degrees.

An attempt was made to prepare diphenyltellurium dichloride in a separate experiment by dissolving the dark red-orange oil obtained in the above experiment in the minimum amount of carbon tetrachloride and treating the solution with excess sulfuryl chloride. However, no precipitation of white needles occurred, nor did any precipitation occur when petroleum ether was added.

A list of the tellurium compounds prepared and their melting points is shown in Table 5.

Preparation of p-Bromocumene

339 grams of cumene and 16 grams of iodine were placed in a 2 liter flask and 1 pound of bromine was added dropwise with stirring. The solution was cooled in an ice bath during the reaction. It is necessary to run the reaction in the hood since considerable HBr fumes are given off during the reaction. The reaction mixture was extracted with dilute sodium carbonate solution until the oil turned light yellow. The oil was washed twice with water, dissolved in ether, and dried over anhydrous sodium sulfate. The oil was then heated to 170 degrees with a water aspirator and violet fumes were given off. The oil was then distilled at atmospheric pressure and the fraction which boiled at 214-217 degrees was kept. The yield of pure p-bromocumene was about 417 grams. (74.3% yield).

Preparation of Tri-p-cumylarsine by the Grignard Reaction

36.0 grams of Mg and 700 ml. ether were placed in a flask and 299 grams of p-bromocumene dissolved in 300 ml. ether was added slowly. After the Grignard reagent was prepared, 72.0 grams of $AsCl_3$ was dissolved in 200 ml. dry benzene and added slowly to the Grignard reagent. Near the end of the addition of the $AsCl_3$ solution a red-brown precipitate formed. The mixture was refluxed for 2 hours and then decomposed in a solution made up of 700 ml. cold water and 50 ml. HCl. A large amount of odorless gas was evolved. The

organic portion was separated from the aqueous portion by means of a separatory funnel and the organic portion was evaporated to about 200 ml. on a hot plate. The residual reddish-brown oil was extracted several times with hot ethyl alcohol. The alcoholic extracts were combined, boiled to a lower volume, and cooled. An oil separated which hardened when left in the refrigerator for several hours. The solid yellowish precipitate was dissolved in hexane and filtered. Some of the hexane was removed by heating and a white precipitate was obtained which melted at 136-140 degrees C. A second recrystallization from ethyl alcohol gave a melting point of 137.5-140.5 degrees C. About 1 liter of hot alcohol is necessary to dissolve 20 grams of tri-p-cumylarsine. A third recrystallization from acetone gave a compound which melted at 140.8-142.8 degrees C. Yield of tri-p-cumylarsine (pure) was 20 grams (11.7% yield).

Preparation of Tri-p-cumylarsine by the Wurtz-Fittig Reaction

130 grams (5.65 gram atoms) of small sliced sodium chunks were placed in a 2 liter, 3 necked flask and covered with 900 ml. of dry benzene. The flask was fitted with a stirrer and a condenser, and a 500 ml. dropping funnel which contained 170 grams (0.94 mole) of $AsCl_3$ and 482 grams (2.42 moles) of p-bromocumene was placed in the third neck of the flask. About 20 ml. of the $AsCl_3$-p-bromocumene mixture was dropped into the flask and the reaction mixture was stirred

and heated on a steam bath until it darkened and boiled spontaneously. The steam bath was removed and the remainder of the $AsCl_3$ mixture was added dropwise with stirring over a period of 1-1.5 hours at such a rate that gentle boiling was maintained. When the addition was complete the mixture was stirred and heated on a steam bath for 12 hours.

The reaction mixture was filtered while hot through a large Buchner funnel and the filtrate was combined with the filtrates obtained from the extractions of the residue with several 200 ml. portions of boiling benzene. The combined filtrates were heated on a steam bath to remove most of the benzene. The flask containing the residual red oil was connected to a water aspirator and heated under reduced pressure in an oil bath for 2 hours at 120-130 degrees C. to remove unreacted starting materials. When cooled, the crude tri-p-cumylarsine solidified to a light yellow solid which melted at 139-142 degrees C. The crude product was washed with 50 ml. of hot alcohol to remove yellowish-orange impurities. The residue was dried and then dissolved in the minimum amount of hot acetone, filtered, and allowed to cool in the refrigerator overnight. Pure white tri-p-cumylarsine was obtained which melted at 140-142 degrees C.

Preparation of Tri-p-cumylarsine Oxide

80 grams (0.191 mole) of pure tri-p-cumylarsine was dissolved in 650 ml. of acetone and placed in a 2 liter,

3 necked flask with stirrer and condenser. 30 grams (0.26 mole) of 30% hydrogen peroxide was added with stirring over a period of 20-30 minutes. An ice bath was used to keep the temperature of the solution at 30-35 degrees C. during the reaction. After the hydrogen peroxide was added the solution was stirred for 30 minutes and the acetone removed by distillation. The flask containing the residual yellow oil was fitted with a condenser and trap and treated with 100 ml. of benzene. The water was then removed by azeotropic distillation. The process was repeated and white needles of tri-p-cumylarsine oxide began to form upon cooling. The crystals were collected on a Buchner funnel, washed twice with 25 ml. portions of cold benzene, and recrystallized from benzene-hexane. The melting point of the pure tri-p-cumylarsine oxide was 168-169 degrees C. with decomposition. The yield of pure tri-p-cumylarsine oxide was 65 grams (78.3%) from tri-p-cumylarsine.

55.7 grams (0.124 mole) of tri-p-cumylarsine oxide was dissolved in 500 ml. benzene and added to a Grignard solution prepared from 6 grams (0.25 gram atom) of Mg, 44 grams (0.22 mole) of p-bromocumene, and 200 ml. of dry ether. No precipitate formed and the mixture was stirred for 15 minutes and then refluxed and stirred on a steam bath for 30 minutes. The mixture was allowed to stand overnight and the next day 200 ml. of ether was added and a white precipitate formed. The addition product was hydrolyzed with 100 ml. H_2O and 5

ml. concentrated HCl and the hydrolysis mixture was transferred to a 1 liter, round-bottomed flask with condenser and treated with 500 ml. concentrated HCl. No precipitate was obtained. The tri-p-cumylarsine oxide was apparently reduced to tri-p-cumylarsine by the Grignard reagent.

CHAPTER III

CONCLUSIONS

Affsprung and May (1) said that two factors are important in the use of onium-type compounds as analytical reagents for organic anions, namely the melting points of the derivatives and the solubilities of the salts in water and organic solvents. They also thought that it was possible to change the organic groups attached to the central antimony ion and obtain derivatives with the organic anions that would possess more favorable solubility characteristics and a better range of melting points. If the onium ion is symmetrical the derivatives have higher melting points, and para-substituted phenyl groups in onium-type compounds have been shown to form derivatives with higher melting points than compounds with meta-substituted phenyl groups (36).

From the position of tellurium in the periodic table it was predicted that triaryltelluronium chloride would be a suitable reagent for the determination of organic and inorganic ions. During early experimentation with this compound, however, an article by Matsuo and Shinagawa (37) appeared which revealed that the derivatives of triphenyltel-

luronium ion were too soluble to permit the direct use of the reagent as an analytical reagent.

It was next thought that from the position of bismuth in the periodic table tetraarylbismuthonium compounds might be suitable as analytical reagents for organic and inorganic anions. An attempt was made to prepare tetraphenylbismuthonium chloride from triphenylbismuthine dichloride and phenylmagnesium bromide but a purple color was observed and no tetraphenylbismuthonium halide was obtained. The purple color observed in this reaction is interesting and suggests that a kinetics study might prove fruitful. Wittig and Clauss (75) prepared tetraphenylbismuthonium chloride by the decomposition of pentaphenylbismuth and observed that it decomposed at room temperature to triphenylbismuth and chlorobenzene.

Since the increase in molecular weight of the central metal ion did not produce the desired solubility behavior, the molecular weights of the groups around the central ion were increased in the hopes of obtaining a reagent with the desired solubility characteristics. In the effort to develop a stibonium reagent which would form extremely insoluble precipitates with the organic acids, the synthesis of tetra-p-tertiarybutylbenzenestibonium sulfate was attempted. This reagent would have a molecular weight of 1405 compared to a molecular weight of 956 for tetraphenylstibonium sulfate, and therefore might form very insoluble precipitates

with the organic acids. Tri-p-tertiarybutylbenzenestibine dichloride was reacted with p-tertiarybutylbenzenemagnesium bromide but the addition product was insoluble in all acids, water, benzene, and ether. An attempt was also made to prepare tetra-p-biphenylstibonium sulfate, but it is believed that compounds with such high molecular weight as the two mentioned above will be too insoluble to use as analytical reagents.

Tetraphenylarsonium chloride has been used for the determination of a number of inorganic anions and metal complex ions, but the large majority of the derivatives of this reagent are too soluble to permit the use of the reagent for the qualitative or quantitative analysis of these derivatives. Tetraphenylarsonium ion does not form the insoluble hydroxide in basic solution, so it was thought that perhaps a higher molecular weight arsonium ion would form more insoluble precipitates with certain anions. An attempt was made to prepare tetra-p-cumylarsonium chloride and tetra-p-tolylarsonium chloride, but only very small yields were obtained. The para-substituted phenyl groups cause a considerable change in the properties of the arsenoorganic compound. For instance, triphenylarsine oxide, which is one of the starting materials for the preparation of tetraphenylarsonium chloride, does not form a hydrate when exposed to the atmosphere. However, Carson and Wong (13) report that tri-p-tolylarsine oxide is very hygroscopic and quickly becomes sticky when exposed to the

atmosphere. This behavior has been observed for both tri-p-cumylarsine oxide and tri-p-tolylarsine oxide in this laboratory. No explanation has been offered by Carson and Wong as to why tri-p-tolylarsine oxide forms the hydroxide or hydrate and triphenylarsine oxide does not. Blicke and Cataline (8) prepared a number of tetraarylarsonium compounds by the reaction of triarylarsine oxide with arylmagnesium bromide, and reported that in many cases only gummy products were obtained. Small yields of tetra-p-tolylarsonium iodide were obtained by reacting tri-p-tolylarsine with p-bromotoluene and anhydrous aluminum chloride, boiling the mixture with Norite, filtering, and treating the filtrate with potassium iodide according to the method of Mann and Watson (36).

A new reagent, tetra-p-tolylstibonium sulfate, was synthesized and found to be very good for the qualitative identification of a large number of organic acids and a number of inorganic anions. The derivatives are easily prepared and purified. Some of the advantages of these derivatives are: They are prepared from a water solution, whereas a majority of the organic acid derivatives cannot be made from water solutions (24). Of the salts prepared, the melting points are sufficiently far apart for identification. Very simple equipment may be used. The reactions are instantaneous. As may be seen a large number of different types of salts may be prepared, including those of the aromatic sulfonic acids, all of which give good melting points. The

formate, oxalate, and fumarate salts decompose at their melting points with the evolution of a gas; however, the decomposition apparently takes place after the compound has melted, since the melting points are quite sharp.

It was not considered necessary to analyze all of the salts since the precipitates formed rapidly, which indicates an ionic reaction, and there are practically no other products possible from the reactants. In general, the melting points of the tetra-p-tolylstibonium derivatives are slightly higher and the solubilities are lower than those of the tetraphenylstibonium ion. Also, tetra-p-tolylstibonium sulfate is effective in the preparation of derivatives from water solution of the low molecular weight aromatic sulfonic acids. A comparison of the melting points and solubilities of the same organic acid derivatives of tetra-p-tolylstibonium and tetraphenylstibonium ions is given in Table 6.

One of the outstanding advantages of the tetra-p-tolylstibonium derivatives is the desirable range of melting points reported for the large number of derivatives. None of the derivatives melt at less than 100 degrees C. and yet none of the derivatives melt higher than 240 degrees C. As can be seen in Table 7, many of the amide and ester derivatives melt at temperatures less than 100 degrees C. which means that it is difficult to dry these derivatives, particularly when the derivatives are recrystallized from water or

TABLE 6

Comparison of Melting Points and Solubilities of Some Tetraphenylstibonium and Tetra-p-tolylstibonium Derivatives

Salt	Melting Points		Solubilities	
	1	2	1	2
Formate	121	111	0.85	1.32
Acetate	133	158	1.10	0.40
Propionate	135	120	0.55	0.39
Benzoate	162	171	0.09	0.036
Hydrogen Oxalate	229-233	236		
Chloroacetate	135-137	122		
n-Butyrate	106	128		
Isobutyrate	112	124		
n-Valerate	94	108		
Isovalerate	121	126		
Hydrogen Phthalate	181	178		
Salicylate	175	195		
o-Toluate	165	131		
m-Toluate	154	182		
p-Toluate	187	193		

1. Tetraphenylstibonium salts

2. Tetra-p-tolylstibonium salts

TABLE 7

Melting Points of Derivatives of Organic Acids

Acids	Amides*		Esters			Salts**	
	1	2	3	4	5	6	7
Formic	53	50	31	74	135	121	111
Acetic	147	114	78	111	85	133	158
Propionic	124	106	31	102	63	135	120
n-Butyric	75	96	35	89	63	106	128
Isobutyric	109	105	--	89	77	112	124
n-Valeric	74	63	--	69	75	94	108
Isovaleric	107	110	--	76	68	121	126

1. p-Toluidide 2. Anilide 3. p-Nitrobenzyl ester 4. p-Phenylphenacyl ester 5. p-Bromophenacyl ester 6. Tetraphenylstibonium salt 7. Tetra-p-tolylstibonium salt

* Cannot be made in water solutions

** Melting Points given in round numbers

from ethanol and water. Some derivatives of the tetraarylarsonium, tetraarylphosphonium, and triaryltin ions melt at high temperatures, which usually means that sharp, accurate melting points cannot be obtained. Also, it is inconvenient to take melting points at high temperatures.

Although all of the tetra-p-tolylstibonium derivatives melt within the 100-240 degree range, the melting points are not "bunched together" like those of the salt derivatives shown in Table 8 but are spread over a wide range so that very little confusion will occur concerning identity of the derivative. As might be expected, most of the aromatic acid derivatives melt at higher temperatures than those of the aliphatic series.

Some of the disadvantages in the use of tetra-p-tolylstibonium sulfate in the qualitative identification of organic acids are: The reagent cannot be purchased at the present time and must be prepared. Tetraphenylarsonium chloride may now be bought commercially; therefore it is probable that when there is more demand for tetra-p-tolylstibonium sulfate it will also be prepared commercially. The reagent is not difficult to prepare and fairly good yields are obtainable in all steps of the syntheses. Another disadvantage is the fact that the reagent forms the insoluble hydroxide at pH's higher than 7.0. Some of the higher molecular weight aromatic acids are quite insoluble in acid solution so that it was difficult in some cases to avoid precipitation of both

TABLE 8

Melting Points of Salt Type Derivatives of Organic Acids

Salt	Benzyl Thiouronium	Phenyl Hydrazonium	Piperazonium	Tetraphenyl Stibonium	Tetra-p-tolyl Stibonium
Formate	146	143	---	121	111
Acetate	134	129	209	133	158
Propionate	148	157	124	135	120
n-Butyrate	146	102	121	106	128
Isobutyrate	148	140	90	112	124
n-Valerate	---	109	113	94	108
Isovalerate	153	---	139	121	126

the tetra-p-tolylstibonium reagent as the hydroxide and the organic acid. However, if a very pure reagent is used, no precipitation of the reagent will occur at a pH of less than 7.

A polarographic method was developed for the equivalent weight determinations of the water-soluble organic acids, and this method serves with the reported melting point of the organic acid as a double check on the identity of the acid. As mentioned above, some of the high molecular weight aromatic acids were insoluble in sulfuric acid solution, so that some of the equivalent weights of these derivatives could not be obtained by the polarographic method. However, it was quite simple to obtain the solid aromatic acid from the original organic acid solution, and the melting point of the solid organic acid served with the melting point of the tetra-p-tolylstibonium derivative as a double check on the identity of the organic acid.

The precision obtained in the polarographic determination of the tetra-p-tolylstibonium derivatives as calculated in Table 4 compares favorably with the precision reported by other workers for the polarographic determination of other materials. The factors influencing the variables of the Ilkovic equation were analyzed by Taylor and Buckley (70). They concluded that with reasonable control of the experimental conditions values of the diffusion current constant can be determined with a precision of $\pm$ 2%. The use

of this constant in the Ilkovic equation permits, under a similar control of conditions, the calculation of the concentration to the same precision.

The precision obtained in our work is satisfactory when it is taken into account that only ten milligrams of the tetra-p-tolylstibonium derivative is necessary for an analysis. One of the advantages in using polarography for the equivalent weight determination of the tetra-p-tolylstibonium derivatives is that only small amounts of material are required for analysis. Considerably larger amounts of material would be required if it were necessary to obtain better precision in the analysis of the derivatives by another method.

The polarographic method is considered to be superior to carbon-hydrogen analyses for the determination of tetra-p-tolylstibonium derivatives, since carbon-hydrogen analyses do not qualitatively identify the derivatives. The tetra-p-tolylstibonium ion can be qualitatively identified in polarographic analyses by its half-wave potential which occurs at -0.66 volts vs. the saturated calomel electrode.

Commercial microanalytical laboratories achieve a precision of about $\pm$ 0.5% in carbon analyses. As can be seen in Table 3, several of the theoretical carbon percentages of the tetra-p-tolylstibonium derivatives are so close together as to be within the margin of experimental error for a carbon analysis. For example, the theoretical carbon percentage

for tetra-p-tolylstibonium acetate is within 0.52% of the theoretical carbon percentage for tetra-p-tolylstibonium formate and within 0.49% of the theoretical carbon percentage for the propionate. The theoretical percentage of tetra-p-tolylstibonium in tetra-p-tolylstibonium acetate is within 2.36% of the theoretical tetra-p-tolylstibonium percentage of the formate and within 2.23% of the theoretical tetra-p-tolylstibonium percentage of the propionate, so the polarographic method is considered to be as good or better than carbon analyses for the identification of tetra-p-tolylstibonium derivatives.

The precision obtained by commercial laboratories for hydrogen analyses is about ± 5%, which means that hydrogen analyses are practically useless for the identification of tetra-p-tolylstibonium derivatives.

Buckley and Taylor (70) state that the normal precision of a polarographic analysis is ± 2%. The precision in weighing ten milligrams of derivative is no better than 1%, since materials cannot be weighed on the analytical balance more precisely than ± 0.1 milligram. Therefore the minimum experimental error for polarographic analyses is ± 3%. If consideration is made of the pipetting errors in preparing solutions of the derivatives, the minimum error is slightly more than ± 3%. The precision for our analyses is somewhat less than ± 3%.

Tetra-p-tolylstibonium sulfate has all of the advantages that tetraphenylstibonium sulfate has for the qualitative analysis of organic acids plus a wider application. It also appears that the reagent can be used for the quantitative analysis of some of the acids which give the more insoluble salts. Finally it may be said that the salts of the organic acid and tetra-p-tolylstibonium ion precipitate from dilute solutions with a minimum of preliminary preparations. The derivatives are stable, insoluble in water, and easy to recrystallize.

In conclusion, it may be said that tetra-p-tolylstibonium sulfate is the best reagent for the qualitative determination of organic acids at the present time. No other reagent for the determination of organic acids can compare with the advantages of this reagent for the qualitative identification of organic acids.

The polarographic method developed is considered to be superior to C-H analyses for the determination of tetra-p-tolylstibonium derivatives. A polarographic analysis, along with the melting point data, serves as a double check on the identity of an organic acid. In nearly all cases the melting or decomposition points obtained are sufficiently sharp and far enough apart for the identification of many organic acids.

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