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Inorganic Analysis with Organic Reagents[1]

JOHN H. YOE AND LANDON A. SARVER

The purpose of this paper is to outline and discuss briefly the various ways in which organic compounds may be used in inorganic analysis. The use of organic reagents in analysis is almost as old as analytical chemistry itself, yet comparatively few workers at the present time possess more than a superficial knowledge of their advantages and possibilities. Indeed, in the United States at least, the growing tendency towards specialization has seemed to limit more and more the number of those who are trained both in organic and in analytical chemistry, with its numerous ramifications in the physical and inorganic fields.

It is not necessary for organic reagents to be superior to inorganic ones as a class, in order that their study should be considered important; it is enough that in many cases they can do what inorganic substances cannot do, or that they can do a given thing better. As a first consideration, the great number and the variety of organic compounds increase the probability of finding superior reagents for many purposes; already, more than six hundred compounds of carbon have been recommended for use in analysis in one way or another. It was not to be expected that a majority of these would come into general use, but, nevertheless, a considerable number have achieved conspicuous success. For example, by conventional methods iron must be precipitated from alkaline solution; but cupferron does this from an acid solution, thus effecting some otherwise difficult separations.

ORGANIC SOLVENTS AND WASH LIQUIDS

In the matter of solutions themselves, we are practically limited to water among inorganic substances. Liquid ammonia for instance, could not be considered a convenient reagent; but in the organic field, the opportunities are greatly multiplied. We are able to separate salts by differential solubilities in alcohols, ethers, esters, and ketones when they defy resolution in strictly aqueous media.

The use of organic compounds as solvents or wash liquids, where their functions are physical rather than chemical, is very

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[1]This paper was not presented at the 1941 Symposium on Organic Analytical Reagents but is being included in this issue of THE VIRGINIA JOURNAL OF SCIENCE because of its general treatment of the subject.

widespread; yet, at the same time, it cannot be said that a great deal of ingenuity has been shown so far in the employment of new substances or in devising new methods for using the old. One of the earliest recorded uses of an organic reagent in quantitative analysis was the observation of Sérullas in 1831 that potassium perchlorate may be separated from sodium perchlorate by extraction with ethanol; and since that time a great volume of work has been done in the study of this and other extraction methods.

Organic liquids may be used in the laboratory for various physical purposes : (1) those which are miscible with water may serve for the washing of vessels and precipitates, and (2) certain low boiling ones may be used for the drying of vessels and precipitates; (3) when added to aqueous solutions of salts, organic liquids frequently change the activities of some ions to a greater extent than they do others, thus reducing the solubility of a given salt and giving a cleaner separation of it from other accompanying substances—e. g., the precipitation of lead sulfate and calcium sulfate in the presence of ethanol; (4) in much the same way organic liquids may serve in dry extractions; (5) likewise, by their effect on the ionic activities in solution, organic liquids assist in the displacement of chemical equilibria in favor of complexes or undissociated colored molecules, and in numerous cases they increase the sensitivity of color reactions, as with ferric and cobaltic thiocyanates upon the addition of ethanol or acetone; (6) reagents, especially organic ones, are frequently employed in the form of a solution in an organic liquid, and the same liquid may be used in the subsequent removal of an excess of the reagent; (7) organic liquids which are immiscible with water are often extremely useful for extracting and concentrating some constituent into an upper or lower layer, especially in the case of color reactions; (8) immiscible liquids may also be used for protective layers, to reduce the rate of evaporation or prevent atmospheric oxidation; (9) likewise, organic liquids may be used as aids in distillation, as in the use of hydrocarbons for the determination of moisture; and (10) by their effect on the surface tension of aqueous solutions, organic liquids may increase or decrease foaming, or may aid in collecting small quantities of precipitates at interfaces.

Several factors need to be considered in selecting an organic liquid for a given purpose. Primarily, of course, it must perform whatever function is desired, and normally must do so more effectively than any other liquid. Cost and other things, however, must also be considered; intensive efforts have been made to find satisfactory substitutes for ethanol, because of excise taxes and stringent regulations on its use. The boiling-point should be high or low, according to whether the solvent must be removed quantitatively at some stage of the operation or if it is important

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to prevent undue loss by evaporation. The vapor pressure is important not only in connection with evaporation but also in relation to odor and toxicity, since high volatility would be extremely disagreeable in the case of an odoriferous or poisonous substance. Wherever possible, non-toxic compounds with pleasant odors are to be preferred. Although toxicity in the liquid phase would be somewhat less serious, it is nevertheless undesirable. Also related to the vapor pressure is the flash-point, which should be as high as possible in order to reduce the fire hazard. Especially in extraction methods, the specific gravity of the organic solvent should differ appreciably from that of the aqueous solution, in order to obtain satisfactory separation of the layers. In certain cases, the refractive index and the dielectric constant may also be of interest.

ORGANIC ACIDS AND BASES

Organic acids and bases are often used for the adjustment of the hydrogen ion concentration of aqueous solutions, being superior to ammonia, the alkalies, and the mineral acids for this purpose. Both they, and their salts, are widely employed as standards and in the preparation of buffer solutions. Since many of them also undergo molecular rearrangement with change of color upon dissociation, they are extremely valuable as hydrogen ion indicators. In addition to their neutralizing function, organic acids and bases may act in any one of several other ways: (1) they may precipitate insoluble normal salts, such as calcium, strontium, or barium oxalates; (2) they may tie up certain ions as soluble complexes, as in the case of aluminum and tartaric acid; or (3) they may serve as reducing agents, as in the reaction between permanganate and oxalate ions, or in the use of certain dyestuffs for the colorimetric detection and estimation of oxidants.

ORGANIC OXIDIZING AND REDUCING AGENTS

The number of organic reducing agents is enormous. By this action, a metal or compound may be precipitated, sometimes as a colored colloidal suspension suitable for quantitative comparison with standards. In other cases, a soluble colored ion may result, which is still better. Or, the organic oxidation product itself may be colored, and serve for the detection or quantitative determination of an inorganic ion by direct means. A smaller, but important, group of organic compounds act as oxidizing agents. And either oxidizing or reducing substances may be employed as oxidation-reduction indicators, whenever the two forms have different colors. Often the color changes are reversible.

INDICATORS AND OTHER AIDS

The great majority of indicators employed in volumetric analysis are organic compounds; in fact the end-points in each of

the three types of volumetric analyses are usually determined by use of an organic indicator. We may divide these indicators into three classes:

1. Hydrogen ion indicators—for acidimetric and alkalimetric titrations, and for pH determinations.
2. Indicators for oxidation-reduction titrations.
3. Indicators for precipitation titrations.

A considerable number of organic compounds act as adsorption indicators, as with dichlorofluorescein in the titration of a chloride by silver nitrate. Others diminish adsorption or post-precipitation of unwanted ions, as is the case with certain aldehydes in the precipitation of copper and zinc sulfides; while still others, notably proteins, delay the coagulation of precipitates, and act as protective colloids in colorimetric and nephelometric determinations.

CHELATE COMPOUNDS

But the most interesting organic reagents of all are those which form a ring containing a metal, the products being known as *chelate* compounds or *inner-complex* salts. The chelate compounds were so named by Morgan because of the imagined structural resemblance to the great claws of the lobster, crab, and other crustaceans (Greek χηλή = claw). While, in the majority of cases, the metal is united to the rest of the compound by two arms, or bonds, a full consideration of these substances requires their classification into unidentate, bidentate, terdentate, and quadridentate compounds, respectively, according to the number of points of union involved. Compounds in which the metal is attached to the body of the substance by one or more coördinate valences differ profoundly, in many of their important properties, from those held together by normal or electrovalences alone. For instance, the electrostatic bond breaks readily in aqueous solution, giving electrically charged ions and conducting solutions. Coördination compounds, on the other hand, do not readily dissociate, and are usually either insoluble or extremely slightly ionized in water; the reactions, therefore, are generally complete and irreversible. They differ, too, from normal inorganic salts in being soluble in hydrocarbons and other organic solvents; therefore, they may be extracted from aqueous solutions, thus being concentrated in a small volume. As a class, they have low melting-points, while those of inorganic salts are high. They are usually quite volatile, sometimes without decomposition, at atmospheric pressure. The metal being determined normally constitutes only a small proportion of the total weight of the chelate compound. Finally, they frequently react in a very selective way with one or, at the most, a very few metallic ions;

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and this is one of the ideal goals of analytical chemistry. This opens up still another promising field of work, namely, the use of organic compounds as concentrating reagents for "trace elements" in spectrographic analysis and studies. Thus, by means of organic compounds that react selectively with certain elements to form slightly soluble precipitates, it should be possible to detect and to measure quantitatively elements at concentrations far below the spectrographic limit, when analyses are made without previously concentrating selectively the constituent in question.

Primary Standards in Volumetric Analysis

Many of our primary volumetric standards are organic compounds. Few substances, if any, completely satisfy all the requirements for an ideal standard. Generally a compromise between the various requirements must be made, although several organic substances approach the ideal very closely. Organic compounds offer a wide variety from which to choose; a number of these have been thoroughly investigated and are now extensively used. Some are not so satisfactory from the standpoint of the ideal and yet may serve as useful standards under well-defined conditions.

The Salinogenic Reagents

As already mentioned, many organic substances possess acidic or basic properties. Because they influence the hydrogen ion concentration of solutions they are widely used as regulators of pH, and in the preparation of buffers. This is by no means their only function, however, and organic acids and bases may also form salts or complex ions with inorganic ions or salts. Those compounds which are capable of acting in this way, either by replacement of hydrogen or hydroxyl ions or by direct addition of uncharged molecules, may be called "salinogens" or "salinogenic reagents", because of this property.

The more common types of salts, which usually dissociate largely in solution (e. g., calcium, strontium, or barium oxalates), are known as "true" salts, and when such compounds exist at all as undissociated molecules, the component parts are held together by electrostatic forces. When, on the other hand, at least some of the parts are held together by covalent forces, and are capable of existing independently under other conditions (e.g., the pyridine-thiocyanate complexes), they may conveniently be described as "coördination-complex" salts, or simply as "complex" salts; they may, or may not, be "true" salts as well, according to whether or not they dissociate in solution to produce electrically charged ions (e. g., K_2PtCl_6 is an electrolyte, while $Pt(NH_3)_2Cl_4$ is not). And finally, we have the "chelate" or

"inner-complex" type of salt, which we have already discussed briefly.

In actual practice, the great majority of salt-forming reagents which have so far been discovered are acidic in nature. Fortunately, the field is not limited to the more conventional types of organic acids, because the carboxy-acids yield only a few salts of analytical value; of considerably greater interest are other groups which are capable of splitting off hydrogen ions in solution, with subsequent replacement by metallic ions. It also frequently happens that substances which are not ordinarily considered to be acids, do actually yield small concentrations of hydrogen ions due to keto-enol isomerism, or other types of dynamic isomerism, when the equilibria are disturbed by the presence of certain metallic ions which are capable of forming very slightly soluble or slightly ionized salts.

The most common acidic radical in organic compounds is the hydroxyl, or OH group; it seldom splits off hydrogen ions with any great degree of completeness, but it very frequently does so sufficiently to yield metallic salts. When the carbonyl, or CO group, is interposed between the hydroxyl and the organic radical proper, it will be recognized as the essential part of the familiar carboxyl, or COOH group; and in a similar manner, when N, NO, SO, SO_2, As, or AsO are interposed, we have the oxime (or enolic form of the nitroso group, NOH), nitroxyl (or enolic form of the nitro group, $NO \cdot OH$), sulfinic acid ($SO \cdot OH$), sulfonic acid ($SO_2 \cdot OH$), arsinic acid ($As(OH)_2$), or arsonic acid ($AsO(OH)_2$) groups, respectively. When viewed in this manner, the oxygenated organic acidic groups assume a much smaller degree of complexity.

It is also a noticeable fact that replaceable hydrogen is always attached to a non-metal, and since in the case of an organic compound the non-metal must be interposed between the hydrogen and the organic radical, it must have a valence of at least two; therefore, only a few elements need to be considered. The interposition of nitrogen and arsenic between the hydroxyl and the organic radical has already been mentioned; apparently, antimony and bismuth are too basic in nature to give rise to acidic substances, and in such examples as are known the hydroxyl group splits off as a unit in water solution; phosphorus, on the other hand, does give rise to the corresponding phosphonic, phosphinic, and phosphinous acids, but these have not been investigated as yet from the analytical point of view.

In conclusion, let us emphasize that much experimental work is needed to establish the relationship between the molecular structure of organic compounds and their analytical reactions.

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When a new reaction is discovered, it is then necessary to make an extensive investigation to determine its nature, limits of accuracy, its sensitivity, optimum conditions for its use, the interference of various ions, etc. The vast number and variety of organic compounds offer a most promising field for new and better analytical reagents and amply justify further research.

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Third Symposium on Organic Analytical Reagents

INTRODUCTION

JOHN H. YOE

Today marks the third time our group has met to discuss organic compounds as reagents in inorganic analysis; to make progress reports on investigations being made in the laboratories of the various co-operating institutions; and to present certain topics of special interest to workers in this comparatively new field in chemical analysis. Our group now includes: The College of William and Mary, Hampden-Sydney College, Mary Baldwin College, Randolph-Macon College (Ashland), Tulane University, University of North Carolina, Virginia Military Institute, Virginia Polytechnic Institute, Washington and Lee University, and University of Virginia. We especially welcome our sister institution, the University of North Carolina, whose representative is here in person to take part in today's program. We also greet our friends at Tulane University and regret that distance makes it impractical for them to be with us today in person.

The number of organic compounds investigated by all ten co-operating institutions now totals more than 4,500 and includes a great variety of substances from the standpoint of molecular structure. These studies should lead to a better knowledge of the relationship between the structure of organic molecules and their reactivity as analytical reagents; thus the way should be opened up for the discovery of new specific and highly sensitive reagents in inorganic analysis. During the past year several new and useful organic analytical reagents have been discovered and these are now being critically studied. Reports today from the co-operating institutions will outline the progress that has been made in the respective laboratories since the Symposium held in Lexington last May.

During the past year at the University of Virginia more than 500 compounds have been investigated, bringing the total number examined in this laboratory to approximately 2,400. The reactions of these have followed the general trend of those previously observed; i.e., oxidizing agents, such as Ce^{+4}, Au^{+3}, Fe^{+3}, Ir^{+4}, and VO^{+3}, have been the most reactive; especially Ce^{+4} and Au^{+3} which react in a specific manner with many of the compounds.

About 40 anthraquinone derivatives were included in the studies but were not especially reactive. Their insolubility causes a disadvantageous precipitation of the reagent. Moreover, when

acting as precipitants, these anthraquinone derivatives react with groups, i.e., rare earths, alkaline earths, and many of the other metals, thus affording no specific reaction. About 30 benzoanthrone compounds were tested, and as a class, they are as unreactive as any encountered in our studies.

The studies on the various oximes have been continued and 35 additional oximes were prepared and investigated, about half of them having been synthesized for the first time. Observations have confirmed pervious generalizations as to the reactivity of oximes. Two of the oximes give excellent promise as analytical reagents. Dianisalacetone oxime and cinnamalanisalacetone oxime precipitate tungsten quantitatively in hydrochloric acid medium, yielding bright yellow precipitates that are satisfactory for the gravimetric determination of tungsten. The reagents appear to be specific for the WO_4^{-2} ion.

Sodium catechol disulfonate has been studied as a possible reagent for the detection and colorimetric determination of ferric iron. The purple color formed in acid solution permits the detection of 1 part of iron in 20,000,000 parts of solution; in basic solution the bright red color formed gives a means of determining iron at a concentration of 1 part in 50,000,000.

More than 65 substituted thioureas have been carefully studied. Their reactions were observed and correlated as regards the respective ions. The sensitivity of these compounds as reactants with Cu^{+2}, Bi^{+3}, Pd^{+2}, and Se^{+6} were carefully determined and compared with that of thiourea.

Similarly, about 40 substituted diphenylamines have been investigated and an attempt made to correlate their reactivity with the groups present. The substituted groups included NO_2, NO, NH_2, HO, COOH, OCH_3, SO_3, halogens, etc. Fairly definite conclusions as regards the reactivity of diphenylamines in relation to the groups present may be formulated. Thus, the presence of one or two nitro groups either decreases the reactivity markedly or destroys it entirely; whereas the presence of a hydroxyl or amino group may alter the color of the product formed but does not necessarily decrease the reactivity.

The reaction of 2-thio-5-keto-4-carbethoxy-1,3-dihydropyrimidine with silver was studied in detail. This reagent gives a brilliant purple color with silver which serves as a sensitive colorimetric method for this element, detecting as little as 1 part in 50,000,000 parts of solution. The optimum conditions for the reaction were determined, including the pH, interfering ions, temperature effect, concentration of the reagent, and stability of the colored solution. Spectrophotometric measurements of the transmission of solutions of the silver compound and of the organic reagent were made and optimum conditions established for the visual and spectrophotometric application of the reagent.

The precipitation of zirconium by means of 5-chloro-broma-

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mine acid was studied in some detail. The reagent gives a voluminous, bright red precipitate, but unfortunately no means was found for making the reaction quantitative. The reaction is, however, valuable as a qualitative test for zirconium. Similar studies were made with copper and again resulted in a non-quantitative precipitation of copper.

Recently a compound has been discovered that gives an extremely sensitive reaction with cupric ions. The sensitivity is of the order of 1 part of copper in 20,000,000 parts of solution and the specificity is very favorable. The reaction rate is slow but an attempt is being made to work out a pratical method for the colorimetric determination of small amounts of copper.

UNIVERSITY OF VIRGINIA.

A Progress Report on the Reactions of Organic Compounds with Inorganic Ions

W. J. FRIERSON AND PALMER M. SIMPSON

During this school year tests have been completed on two hundred and fifty organic compounds. Of this number forty-nine reacted, eleven of which were specific tests. Nine indicators were found in this group. It is interesting to note that in the work this year, twenty-eight anthraquinones and sixteen benzoic acids gave no reaction at all. Anthraquinones and benzoic acids were especially selected this year because last year three out of eighteen benzoic acids and ten out of forty anthraquinones gave promising reactions.

Again this year, as last, the element which gave the most reactions was gold with thirty-one reactions recorded. Others reacting most frequently were: silver 16, copper 14, ferric iron 14, osmium 13, tungsten 11, vanadium 10, and palladium 8.

Among the indicators, six had amino groups and four were phenols. One, thiophenanthrone dicarboxy acid, was fluorescent. With two exceptions, all the indicators were yellow in basic solutions and colorless in acid solutions.

Of the specific tests found eight were recorded for tungsten, two for ferric iron, and one for silver. Six of the organic compounds which gave a test for tungsten contained a nitro group.

There were no outstanding results from the standpoint of sensitivity. However, there were some which seemed to have possibilities. For example, dichlorobenzidine gave a green color with gold which was sensitive to about one part in five million. Other compounds gave sensitivity tests of about one or two parts per million.

The two hundred and fifty compounds investigated this year make a total of seven hundred and fifty for Hampden-Sydney. No attempt at present has been made to correlate the structure with the colors or precipitates observed. Next year, the work at Hampden-Sydney will be the thorough investigation of the most promising of the compounds. The most promising one in the seven hundred and fifty appears to be the test for gold using 4-amino-3-methylphenylmorpholine which is sensitive to gold one part in thirty million.

HAMPDEN-SYDNEY COLLEGE.

Bz.2-Oxybenzanthrone and Bz.2-Hydroxybenzanthrone as Acid-Base Indicators

F. H. Fish and W. H. Wrenn

It has been found that Bz.2-oxybenzanthrone and its enol form, Bz.2-hydroxybenzanthrone, may be used as acid-base indicators. Both of these compounds are quite insoluble in water. Six drops of a saturated solution in 48% alcohol is satisfactory for a single titration. The color change takes place at pH 7.4. The indicators are canary yellow in acids and delicate purple in alkalies; dissolved in 48% alcohol both compounds yield yellow solutions.

A solution of each indicator was used in titrations and the precision checked using phenolphthalein and methyl orange. Titrations indicate that either Bz.2-oxybenzanthrone or Bz.2-hydroxybenzanthrone may be used wherever phenolphthalein is satisfactory.

The color change of the indicators is a function of the hydrogen-ion concentration and the conversion (at the end-point) of the keto form to the enol takes place almost instantaneously.

Titration data and several curves, the ionization constant for the indicators, and the effect of carbonates, boiling solutions, and oxidizing agents will be published later in a full report.

Virginia Polytechnic Institute.

β-Resorcylic Acid as a Colorimetric Reagent for Ferric Iron

JEAN L. LARNER AND WM. E. TROUT, JR.

Work has been continued on the study of β-resorcylic acid (2,4-dihydroxybenzoic acid) as a colorimetric reagent for ferric ion. The reagent forms a colorless, stable solution in water, and is apparently unaffected by sunlight. It is readily synthesized, and is obtainable from the Eastman Kodak Company. β-Resorcylic acid forms a red complex with ferric ions, which appears to be stable in sunlight and on standing. The transmission curve shows a peak between $425m\mu$ and $450m\mu$ and rises to its highest value in the red.

At the present time it is convenient to produce the color standards as follows: Suitable volumes of standard iron solutions are added to 100 ml. Nessler tubes, to which are then added 25 ml. of buffer solution (1 part $1\,N$ HCl to 1 part $1\,N$ CH_3COONa) and 1 ml. of saturated β-resorcylic acid solution ($0.017\,M$). The mixture is diluted to the mark. The pH of the solution is 2.9.

The lowest concentration of iron detected under these conditions, using the Yoe Roulette Comparator, is about 1 part in 20,000,000. The favorable pH appears to be between 2.5 and 3.0.

Several salts interfere with the color formation. The interfering ions are to be studied.

MARY BALDWIN COLLEGE.

A Progress Report on the Investigation of Organic Compounds as Reagents in Analytical Chemistry

F. T. LENSE, C. A. GLOVER, AND EDWIN C. MARKHAM

Approximately 700 organic compounds were tested as possible reagents for the metal ions. The most interesting classes of compounds were the chalcones, ketones, and aldehydes from which the chalcones were derived, flavanones, coumarins, sulfonium compounds, derivatives of sulfanilamide, various sulfonyl compounds, and urethanes. Numerous phenols were tested and results characteristic of phenols were obtained.

Without attempting to be specific, a summary is given below showing the most striking characteristics of the above classes of compounds.

Chalcones. Most compounds of this class contained one or more hydroxyl groups and in some cases methoxy and benzoyloxy groups in addition. The chalcones are characterized by a great variety of reactions with metal ions. Some are extremely reactive while others react with only two or three metal ions. No compound in this class was specific, except one which was oxidized by the ceric ion. In general, the chalcones are more reactive than the ketones and the substituted benzaldehydes from which they are made. A study is being made to determine the relationship between structure and reactivity.

Coumarins. A number of the 4-methyl-7-R_1-8-R_2 and 4-methyl-7-hydroxy-8-R_2 coumarins were tested and as a class were found to be unreactive despite the presence of the hydroxyl group.

Pyrylium Compounds. This class of compounds, though very reactive, was so unstable in the presence of either acid or base as to vitiate the results.

Sulfonium Compounds. Salts of the phenyl phenacyl sulfonium series in most cases reacted with one or more of these ions: $AuCl_4^-$, $IrCl_6^{-2}$, Pd^{+2}, $PtCl_6^{-2}$, Ag^+, $RhCl_5^{-2}$. It was interesting to note that iridium reacted with 13 of the 15 salts in this class. Rhodium reacted with only one.

Sulfonyl Compounds. Included in this group of compounds are the sulfones, sulfides and sulfonates. Although as a class the sulfonyl compounds are rather unreactive, some unusual reactions were discovered. For example, six of the compounds appear to be specific for osmium. It must be admitted that the purity of the compounds in some cases was doubtful.

Sulfanilamides. Of the 36 N^1 and N^4 substituted derivatives

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of sulfanilamide tested, 16 were found to react with the cupric ion. In several instances, the compounds were oxidized by the ceric ion. In only one instance did a compound of this class react with other metal ions (gold and platinum).

Urethanes. Fourteen compounds of this type were tested and six reacted with Cu^{+2}, $AuCl_4^-$, $PtCl_6^{-2}$ and Pd^{+2}. One reacted with Cu and Au, while four were specific for copper. The other three gave no tests. In all cases in which the cupric ion reacted, a green precipitate resulted, the sensitivity being about 1 p.p.m. One serious difficulty in connection with the use of the urethanes as reagents for colorimetric procedures lies in their low solubility in water.

Some of the compounds tested give promise of being useful in colorimetric analysis and are being investigated.

The authors wish to express their appreciation to Dr. R. W. Bost and Dr. Alfred Russell who furnished many of the compounds tested.

UNIVERSITY OF NORTH CAROLINA.

The Salinogenic Organic Reagents

Landon Arndale Sarver

Although organic substances are frequently used in analysis as solvents, acids, bases, indicators, *et cetera,* the most important and interesting ones are those that form an actual compound with the element or group being determined.[1,5]

Some of them form salts in the true sense of the term, e.g., calcium oxalate. Others give double salts, such as the pyridine-thiocyanate complexes, in which ordinary valence forces do not come into play at all. But by far the most spectacular results have been achieved with a class of substances that are capable of forming closed rings, or *chelate* compounds.[3] In these, the element being determined attaches itself to the organic molecule at two or more different points; most commonly, one of the bonds is formed by replacement of a hydrogen atom, while the other is the result of *coordination;* but both may also be of the latter type.

A new word, *salinogenic*[7], has been coined to designate salt-formation of all kinds, whether the product be a true salt like calcium oxalate, a coordination complex like $Pt[NH_3]_2Cl_4$, or a chelate compound like nickel dimethylglyoxime. It thus embraces salt-like substances as well as true salts, and the reagents may be either acidic or basic in nature.

In actual practice, the great majority are acidic, and the reaction is initiated by the replacement of a hydrogen ion by a metal. Fortunately, the field is not limited to the more conventional types of organic acids, because the carboxylic acids yield only a few salts of analytical value; of much greater importance are other groups that are capable of splitting off hydrogen ions, even though their degrees of dissociation may not be very great. Some compounds that do not appear at first glance to be acids at all, do in fact ionize to a slight extent as a result of dynamic isomerism.

Briefly, it can be expected that hydrogen may be replaceable if it is attached to oxygen, sulfur, or imino nitrogen. The hydroxyl group is important not only in alcoholic and phenolic compounds, but also in a number of other familiar larger radicals, where it constitutes the essential working part. Thus, the interposition of carbonyl between the hydroxyl and the main body of the molecule yields the carboxy group; while the interposition of N, NO, SO, SO_2, As or AsO give rise to the oxime or enolic form of the nitroso group, nitroxyl or the enolic form of the nitro group, sulfinic acids, sulfonic acids, arsinic acids and arsonic acids, respectively. Apparently, antimony and bismuth do not act in an analogous manner to arsenic; but phosphorus does give rise to organic phosphonic, phosphinic and phosphinous

acids; the analytical properties of these latter have not yet been investigated.

Mercapto compounds are frequently more highly dissociated than the corresponding hydroxyl compounds, but fewer examples are known. Here, too, the interposition of other groups between the mercapto part and the body of the molecule gives rise to other acidic groups; for example, the interposition of CO yields monothiocarboxylic acids, while CS gives dithiocarboxylic acids and CS_2 produces trithiocarboxylic acids. Other theoretically possible acids containing nitrogen, phosphorus, arsenic and sulfur have not yet been investigated.

While nitrogen is frequently supposed to be an exclusively basic element, nevertheless the imino group does split off small quantities of hydrogen ions; and these can be replaced by certain metals, particularly silver and mercury. The best known examples are rhodanine and its derivatives. Corresponding substances, in which the nitrogen has been replaced by phosphorus or arsenic, have not yet been investigated.

The value of an acidic reagent will usually be further enhanced if, in addition to the electrovalent linkage, it can also give rise to a coordinate bond in such a position that the metal becomes part of a cyclic structure. The essential conditions for this are: (1) the element that gives rise to the coordinate bond must be so located in the molecule that the ring which is formed will contain not less than three or four, nor more than seven or eight atoms; the number of such rings containing other than four, five or six atoms is negligible; (2) the element giving rise to the coordinate bond with the metal will be a non-metal possessing at least one unshared pair of electrons in its outer orbit; in practice, it will be either oxygen, sulfur or nitrogen; (3) the metal must be able to act as an *acceptor*, and have space free in its outer orbits to receive a pair of electrons.

The limitation as to the size of ring that can be produced is based upon considerations of Baeyer's "strain theory". The common elements behave as if they were regular tetrahedra, with nuclei at the centers and valence forces diercted towards the apexes; and the natural angle between lines drawn from the center to two apexes will be 109° 28'. When two atoms become united by a single covalent (or directional) bond, the valence forces are exerted along a straight line drawn from the center of one through their two respective coinciding apexes to the center of the other; hence the natural angle between two such adjacent lines will also be 109° 28'. When, on the other hand, two atoms are joined by double covalent bonds, the two tetrahedra are considered to have an edge in common; and the angle between the lines representing the directions of the valence forces will be that between the normal from the center to the common edge and a line from the center to another apex, or 125° 16'.

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Now, the values of the angles of equilateral triangles, squares, pentagons, hexagons, heptagons, and octagons are 60°, 90°, 108°, 120°, 128° 34′ 17″, and 135°, respectively. If, then, a three-membered ring is to be formed, the natural valence angles have to be decreased by 49° 28′ if only single bonds are involved, and by considerably more if even one double bond is present. When both single and double bonds exist in the same ring, it is difficult to say how the necessary deflections will be distributed; and since the values of the covalent radii ought also to be taken into account, it is probable that not all rings of a given number of atoms are entirely identical.

For four-membered rings, the average deflections would be 19° 28′, 27° 22′, and 35° 16′ for structures with no double bonds, and 1 or 2 double bonds, respectively; these values are rather high, and comparatively few such compounds are known.

Only small deflections are required, however, for five- and six-membered rings, and large numbers of such substances are known. For five-membered rings, there would be decreases of 1° 28′, 7° 47′, 14° 6′ for 0, 1 and 2 double bonds, respectively; while for six-membered rings there would be a decrease of 5° 16′ for 3 double bonds, and increases of 10° 32′ and 5° 16′ for 0 and 1 double bond, respectively, with no deflection necessary for 2 double bonds.

Rings containing seven or more atoms are comparatively rare. In order to form a seven-membered ring, increases of 19° 6′, 14° 35′, 10° 5′, and 5° 34′ for 0, 1, 2, and 3 double bonds, respectively; and with eight-membered rings, increases of 25° 32′, 21° 35′, 17° 38′, 13° 41′, and 9° 44′ would be necessary for 0, 1, 2, 3, and 4 double bonds, respectively. It should be remarked, however, that negative strain is of less importance than positive, because it can be dissipated by the departure of certain atoms from the plane; and rings containing as many as thirty-two atoms have actually been prepared.

The preceding calculations are based on the assumption that all the atoms involved behave like regular tetrahedra; but recent work by Pauling[4] indicates that the natural valence angles of oxygen and sulfur are closer to 90° than to 109° 28′. The strain theory has been very useful in explaining certain facts and predicting the discovery of others, but in the present state of our knowledge it must be regarded only as a useful approximation; no doubt it will become exact when all factors have been correctly evaluated. Particularly, it must be remembered that in chelation one of the bonds is formed by the replacement of hydrogen, and that it is therefore an electrostatic, or non-directional one. Certain critical requirements as to the length of this bond and to the magnitude of angular strain will undoubtedly apply, but they will not be so rigid as in the case where all the bonds are covalent.

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The location of the second linkage, which completes the ring, is dependent upon the existence of suitable electronic conditions. The coordinate bond is no different from any other covalent one, except in the manner of its establishment; any covalent bond is created by the sharing of a pair of electrons; normally, each of the atoms furnishes one of the electrons, but stable systems can also be set up when one of the atoms *donates* a pair which the other *accepts*. It happens that nitrogen, sulfur and oxygen all possess one or more unshared pairs of electrons in their usual states of combination, and can therefore act as *donors* if they are so located in the molecule that they can yield rings without too great distortion of their natural valence angles. The only remaining requirement, then, is the presence of an *acceptor* with space for the reception of the proffered pair of electrons.

It is now generally agreed that all the elements are formed from the same basic building blocks, the positive protons and the negative electrons; part of the latter rotate at high velocities in series or orbits at considerable distances from the central nuclei, and while the masses of the atoms are determined chiefly by the number of protons present, the other properties are determined chiefly by the manner in which the rotating electrons are arranged.

On this basis, the elements can be divided into four classes, as follows:

I. Elements which in their normal or unexcited states have no incomplete shells of electrons, according to Bohr's theory of atomic structure, and hence are extremely stable (the rare gases).

II. Elements which in their normal or unexcited states have one incomplete shell of electrons, the outermost of which can easily be lost or completed to an octet, with the formation of ions of the rare gas type.

III. Elements which in their normal or unexcited states have two incomplete shells of electrons and give upon excitation ions that differ markedly from those of the inert gas type (the transition elements).

IV. Elements which in their normal or unexcited states have three incomplete shells of electrons and resemble each other in that all have the same number of electrons in the two outermost shells (the rare earth elements).

Of these four classes, the members of the first are completely non-reactive, the ions of the second have no incomplete shells, and such differences as exist in the fourth group lie so deep in the molecules that analytical differentiation becomes practically impossible. The elements of the second group, however, possess numerous distinctive properties, including the following:

(1) Variable valency to a marked extent;

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(2) Strong tendency to form colored ions;

(3) Strong series resemblance, especially with the end members;

(4) Strong catalytic activity;

(5) Small covalent radii, and small atomic volumes;

(6) Very strong tendency toward the formation of coordinate bonds.

Since a number of different requirements have to be met in order to produce a chelate compound, it is not surprising that some metallic ions will do so with a given reagent while others will not. The chelate nature of a given salt can usually be established by a consideration of the following facts, but unfortunately the necessary studies have been made in only a comparatively small number of cases.

(1) Chelate salts are characterized by high volatility and low melting points.

(2) They are, as a rule, non-electrolytes and do not take part in ionic reactions.

(3) They are either very insoluble in water or very slightly ionized, but soluble in numerous organic solvents.

(4) They have low dielectric constants.

(5) In cases where the necessary data are available, the existence of coordinate bonds and chelate rings can be established definitely by means of a property called the *parachor*.

The parachor[2,6] permits the comparison of molecular volumes at constant surface tension, and the establishment of additive constants for the individual elements, for double, triple and coordinate bonds, and for rings of various sizes. If M is the molecular weight, D the density, and γ the surface tension of the liquid:

$$\frac{M\gamma^{1/4}}{D} = \text{The Parachor}$$

Unfortunately, however, the constants have not been determined generally for the metals because of the lack of suitable liquid substances containing them; therefore, the parachor has not yet been of very much value in analytical research.

The considerations outlined in the preceding pages apply to the basic salinogens as well as to the acidic ones, except that in the former case there is no replacement of hydrogen and no electrostatic bond; both linkages are covalent in nature.

It is impossible to enumerate even a reasonable number of the most important salinogens and to show their structural formulae in the space available for this paper.[7] Some idea of their possibilities in analytical research, however, can be gathered from the fact that more than three hundred known reagents are covered by the classification given below, and that several of them give reactions with sensitivities of the order of one part in a hundred million.

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I. The Acidic Salinogens

A. Hydroxyl group.
    a. Alcohols.
    b. Phenols.
    c. Lake-forming dyestuffs.
    d. Enolizable ketones and diketones.
    e. Dioximes and related compounds.
    f. Acyloin oximes.
    g. o-Hydroxy oximes.
    h. Other oximes (including cupferron).
    i. Acidic nitro compounds.
    j. Nitroso and isonitroso substances.
    k. Hydroxy carboxylic acids.
    l. Carboxylic acids.
    m. Amino acids.
    n. Arsinic acids.
    o. Arsonic acids.
    p. Sulfinic acids.
    q. Sulfonic acids.

B. Mercapto group.
    a. Simple mercapto compounds.
    b. Enolizable sulfur compounds.
    c. Other thio compounds.

C. Imino group.
    a. Simple imino substances.
    b. Enolizing imino compounds.

II. The Basic Salinogens

A. Substituted ammonias.
    a. Amines.
    b. Amides.
    c. Substituted ammonium compounds.

B. Heterocyclic nitrogenous bases.
    a. Pyridine and its homologues.
    b. Other nitrogen ring compounds.

C. Diazonium compounds.
    a. Simple diazonium compounds.
    b. Diazo derivatives of arsonic and sulfonic acids.

D. Special reagents for nitrate and chlorate.
    a. Substituted amines.
    b. Heterocyclic ring compounds (including nitron).

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A Progress Report on Studies in Inorganic Analysis with Organic Reagents

Ira A. Updike, Oscar W. Clarke, Jr., and Richard M. Irby, Jr.

With possibly one exception, our work has not produced any useful reagent but it has given us some interesting experience. The compound which may prove to be useful as a reagent is 1-hydroxy-2-carboxyanthraquinone, $C_{15}H_8O_5$. It gives color changes or precipitates with no less than 53 ions in the various tests with inorganic ions at different pH values. It has been suggested that blocking one or more of these groups by ester or ether formation might make the resulting compound more nearly specific in its reaction with inorganic ions. Such work has been planned.

Randolph-Macon College.

A Progress Report on Studies of Organic Compounds as Analytical Reagents

JOHN ROBERT TAYLOR

A total of 187 compounds have been examined at Washington and Lee. Since the last Symposium report, a series of anthraquinone derivatives were run through the routine tests with over 70 inorganic ions at different pH values but none gave color or precipitation reactions.

A preliminary test of a proposed structure for the ferric ion-phenol colored complex has been made; a report of this work appears in the following "Note".

WASHINGTON & LEE UNIVERSITY.

Note on the Ferric Ion-Phenol Color Reaction

JOHN ROBERT TAYLOR

In a report on the ferric chloride reaction with a number of phenols, Wesp and Brode[1] proposed for the colored substance the anionic structure $Fe[RO]_6^{-3}$, where RO^- represents the anion of the phenol ROH. This structure is analogous to that proposed for the ferrithiocyanate ion by Schlesinger and Van Valkenburgh.[2] The ferrithiocyanate structure has recently been criticized by Bent and French[3] who investigated the complex by a photometric method. An adaptation of the method of these authors was used in the present tests to find some evidence for the Wesp and Brode structure of the ferric phenol complex.

If the colored complex has a composition $Fe_n[RO]_m$, the dissociation constant for the reaction $Fe_n[RO]_m = n[Fe^{+3}] + m[RO^-]$ is:

$$Kc = [Fe]^n \cdot [RO]^m / [Fe_n(RO)_m] \ldots (1)$$

If Kp is the ionization constant of the phenol, then [RO] is:

$$[RO] = Kp.[ROH]/[H^+] \ldots \ldots \ldots (2)$$

Substituting this expression into equation (1) and writing the result in logarithmic form yields:

$$\log[Fe_n(RO)_m] = m \log[ROH] + n \log[Fe] - m \log[H] + \log Kp/Kc$$

If the concentrations of Fe^{+3} and H^+ are now fixed, and a constant ionic strength is maintained, log $[Fe_n(RO)_m]$ should be a linear function of log[ROH], provided the phenol concentration is large enough to be only slightly affected by reaction with ferric ion, so that the formal concentration may be considered the same as [ROH]. The slope of a plot of log $[Fe_n(RO)_m]$ versus log [ROH] should give an indication of the value of m.

In the preliminary tests reported here, two reactive phenols encountered during the routine spot testing were used: meta bromophenol, and alpha naphthol trisulfonic acid. The concentration of the colored body in solutions of varying phenol concentration, was measured in a visual colorimeter by matching with a reference solution of fixed phenol concentration. The concentration of ferric chloride was 0.004 M, and was the same in all solutions. The 0.01 M hydrogen ion concentration was checked potentiometrically, and was the same in all solutions. The total ionic strength was adjusted in all solutions to a value of 0.3 by addition of the required amount of sodium chloride. The incident light was passed through a filter transmitting a 15 $m\mu$ band at 515 $m\mu$.

In the plot of results, Fig. 1, the concentration of the phenol was expressed as a fraction of the phenol concentration in the reference solution. Concentration of the colored body was ex-
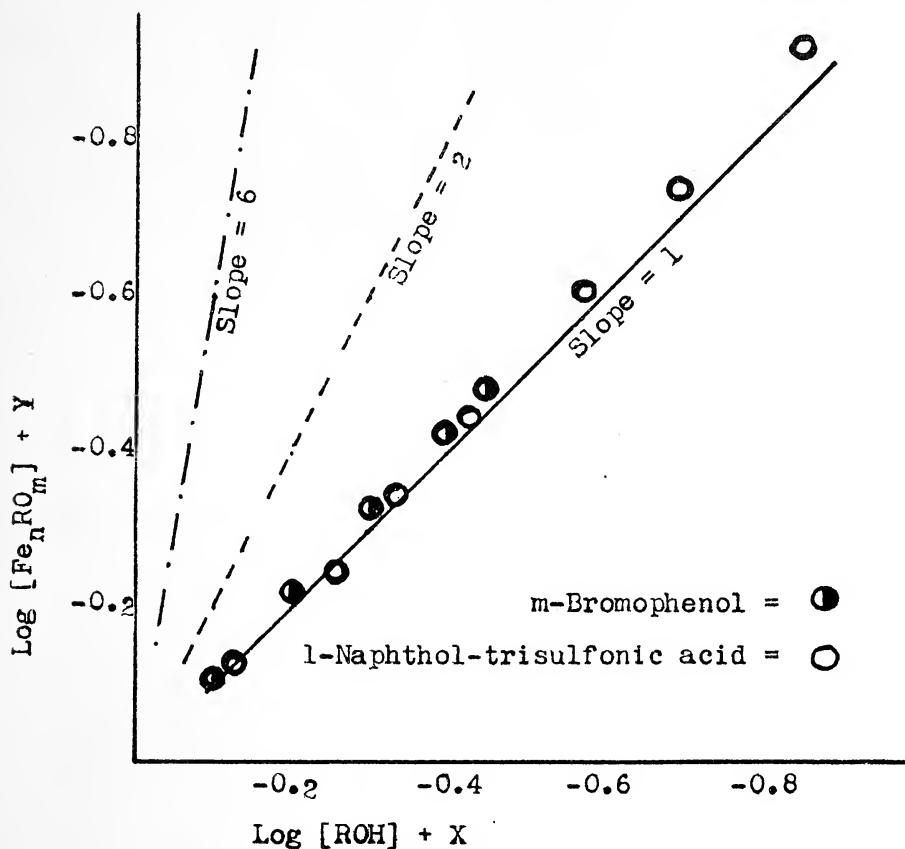

$$\text{Fig. 1}$$

pressed also as a fraction of its concentration in the reference solution, that is, as the ratio of the colorimeter scale reading to the scale reading of the reference solution. The full line has a slope of 1. The experimental points can be seen to fall close to this line, rather than to the broken line of slope 6. Consequently for both phenols, $m = 1$ approximately. If it is assumed that the complex contains a single iron atom $[n = 1]$, the structure of the complex appears to be $Fe[RO]^{+2}$, or possibly $Fe[ROH]^{+3}$.

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Summary

Preliminary tests, using a colorimetric method, indicate that the colored ferric ion complex of m-bromophenol (and of naphthol-trisulfonic acid) has the structure of $Fe[RO]^{+2}$ where RO^- represents the anion of the phenolic compound.

Further work is now in progress at this laboratory on similar complexes of simpler phenols, and a more detailed report of results will be made later.

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Washington & Lee University.

Some Complex Compounds of Copper, Silver and Mercury with Ethanolamines

James W. Cole and M. Brooks Shreaves

A systematic investigation has been made of reactions of mono-, di- and tri-ethanolamines with salts of copper, silver and mercury. In the case of copper, crystalline salts were obtained of the type, $[Cu(ethanolamine)_m]X$. The values of m were, three for the monoethanolamine and two for the di- and tri-ethanolamines, when X was the sulfate ion. When X was chloride ion, compounds with m equal to one were also obtained. In the latter cases chlorine and/or water appeared to be in the cation.

In aqueous solution, the value of m appeared to be influenced by the pH of the solution since definite color changes occurred with variation of pH. Migration of color boundaries under electrolytic conditions and complete precipitation of anions support a structure containing ethanolamine in the cation.

Application of electronic theories of valence and manipulation of molecular scale models (Fisher-Hirschfelder) led to the conclusion that the functional groups of the ethanolamines (N and OH) formed chelated rings with Cu^{++} as a central ion. In the solid crystalline compounds the coordination number of Cu^{++} toward the functional groups appears to be six.

Attempts to prepare complex ethanolamine salts with silver and mercury ions in aqueous solutions resulted in reduction of the ions to the free metal and formation of complex organic metallic substances of uncertain composition. Hot concentrated solutions of the ethanolamines reduced Cu^{++} to Cu^+ and to elementary copper and also formed amorphous organic copper compounds of variable composition.

University of Virginia.

A Progress Report on Inorganic Analysis with Organic Reagents

E. Louise Wallace and Alfred R. Armstrong

Since the Second Symposium held last May, seventy-four organic compounds have been tested by spot-plate technique with seventy-odd inorganic ions at different hydrogen ion concentrations. Ten compounds showed acid-base color changes and nine gave color reactions with certain of the inorganic ions, eight reacting with auric ions. None of the color reactions, however, appear to be sufficiently sensitive to be of value in analytical chemistry.

No attempt has been made to correlate the various structures of the organic compounds and their reactivity with inorganic ions. With an increasing number and variety of substances tested, correlation studies should be helpful in predicting possible new analytical reagents.

COLLEGE OF WILLIAM AND MARY.

A Progress Report: The Reaction between Silver and Guanidyl Thiourea Carbonate

THOMAS B. CRUMPLER AND EARL B. CLAIBORNE

To date 32 compounds have been investigated. Twenty-five of these were supplied by Dr. Yoe. The remaining seven were selected from a collection of compounds prepared by advanced organic students in this Laboratory.

Eighteen of the compounds showed no reaction with any of the seventy-odd inorganic ions. Thirteen compounds reacted with five or more ions but showed no promise as reagents.

The only reaction deemed worthy of further study was that between silver and guanidyl thiourea carbonate, $C_5H_{14}N_8O_3S_2$. A yellow color is produced which can be differentiated from a blank with a silver ion concentration as low as 0.4 p.p.m. in a 50 ml, tall form, Nessler tube. The color attains maximum development in 5 minutes and when stabilized with ghatti gum remains unchanged for a week. Without ghatti gum, the color changes after 24 hours and eventually a brown precipitate settles out. The optimum condition for the reaction is in 0.1 N sodium hydroxide solution with an ammonium hydroxide concentration of 0.1 N. In the absence of ammonium hydroxide, a turbidity develops in solution with silver-ion concentrations above 5 p.p.m. The color fails to obey Beer's law. Temperature variations from 20-30°C show no effect on color. Matching is most sensitive in the range of 1-12 p.p.m. of silver. Copper, mercury (both valences), lead, cadmium and bismuth interfere and should be absent. Analyses were performed in which silver was separated from mixtures by precipitation as chloride in hot solution, subsequently centrifuging and dissolving the preciptate in ammonia. The soluble complex can be treated with the reagent and the color developed. The color is independent of ammonia concentration provided it is at least 0.05 N. Duplicate analyses of National Bureau of Standards Cast Bronze 52a yielded identical results, namely 0.010% Ag. This is in good agreement with the average value of 0.009% given by the certificate of analysis.

Ultramicroscopic examination of the product of the reaction between silver and guanidyl thiourea shows the presence of colloidal particles. Photomicrographs clearly indicate that the colored product is neither silver sulfide nor a compound with thiourea. While the possibility of its being colloidal silver[1] is not completely excluded by the present evidence, it seems likely

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[1]In subsequent experiments, it was observed that when the yellow color was developed in the absence of ghatti gum, the brown precipitate which settled out after ten days proved to be metallic silver. This indicates but does not prove conclusively that the yellow color first developed is due to colloidal silver. In this cnnection see the note on "Silver", Yoe, "Photometric Chemical Analysis", Vol. I (Colorimetry). p. 683, John Wiley and Sons, New York, 1928.

that it is a colloidal suspension of a compound of silver with guanidyl thiourea of the type:

$$NH_2-C-NH-C-NH_2$$

with N⁻ and S below the first and second carbons respectively, both linking to Ag⁺ below.

$$NH_2-\underset{\underset{\displaystyle N^-}{\|}}{C}-NH-\underset{\underset{\displaystyle S}{\|}}{C}-NH_2$$
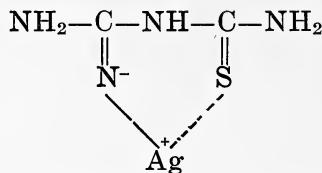
Feigl states that the $=N-H$ group is a silver binding group and the adjacent sulfur offers the possibility of ring closure by co-ordinate linkage, to produce a stable, six-membered ring.

In a separate project which was supported by a research grant from the American Association for the Advancement of Science through the New Orleans Academy of Sciences, 49 amines were investigated. These were tested with the following group of ions: Cr^{+3}, Fe^{+3}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, $RhCl_5^{-2}$, Pd^{+2}, Ag^+, Cd^{+2}, $PtCl_6^{-2}$, $AuCl_4^-$, and Hg^{+2}. These ions show maximum activity in forming ammonia complexes. Several reactions of possible future interest were observed. The most significant generalizations were that amines with OH groups in the side chains and amines with several NH_2 groups (i.e., polyamines) give the deepest colorations with copper, cobalt, etc. Tri-isopropanolamine and triethylene tetramine are the most sensitive reagents for copper that were tried, being respectively twice and three times as sensitive as ammonia. The search for other amines of these two classes is being continued. In addition, it was found that several slightly soluble di- and tri-substituted amines with butyl and amyl side chains form blue complexes with copper; the complexes are far more soluble in undissolved excess of the amine than in water. This appears to offer a delicate and highly efficient means of separating copper in the form of a highly colored complex concentrated in a small volume. A micro-colorimeter is being developed for the further study of these reactions.

TULANE UNIVERSITY OF LOUISIANA.

A Progress Report on Inorganic Analysis with Organic Reagents

W. E. CLARK AND L. R. STALLINGS

Nineteen organic compounds have been investigated during the past year for color reactions and for distinctive precipitates when tested on spot-plates with about seventy-five inorganic ions. Reactions which show some possibility of practical use included the following:

(1) 4-Amino-4'-hydroxy-diphenyl sulfide gives a lavender color with the hypovanadous ion in concentrations as low as 0.2 mg. per ml. The color shows up in still weaker solutions if allowed to stand for 15-20 minutes.

(2) 4-Amino-4'-hydroxy-diphenyl sulfide gives a bright yellow color with palladous ions. When compared with a blank, the color could be readily detected in a solution which contained 5 γ of Pd per ml.

(3) Furo-acetyl-2,5-diethoxy aniline in acetone gives a yellow color with 0.03 mg. of uranium (as uranyl ion) per ml. This is the only intense color produced by the reagent, and consequently it would appear to be relatively free from interference due to other cations. It should be studied as a possible qualitative test for uranyl ion.

(4) 2-Methoxy-4-nitro-phenyl acetate shows some possibility of being a useful acid-base indicator. It changes from colorless in acid to yellow in basic solutions.

VIRGINIA MILITARY INSTITUTE.

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