ORGANIC REAGENTS

JOHN F. FLAGG

ORGANIC REAGENTS
USED IN GRAVIMETRIC AND VOLUMETRIC ANALYSIS

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PREFACE

The advances made in the study and use of organic reagents in the past three or four decades are well known to the analytical chemists. The entire field of inorganic analysis with the aid of organic compounds is indeed now vast, including as it does the many reagents used in qualitative and quantitative analysis, as well as numerous compounds used in more or less incidental fashion as adjuncts in inorganic analysis.

There can be no doubt but that the popularity of organic reagents is deserved. Their accomplishments are outstanding, their potentialities unlimited. The whole of present day analysis, qualitative and quantitative, is replete with methods using organic reagents for specific precipitations, sensitive detections, or the like.

Nor has descriptive literature in the field been lacking. Excellent and comprehensive treatises have been written, including those by Feigl (*Qualitative Analysis by Spot Tests*; *A Manual of Spot Tests; Specific and Special Reactions*), Mellan (*Organic Reagents in Inorganic Analysis*), Prodinger (*Organic Reagents Used in Inorganic Analysis*), and by Yoe and Sarver (*Organic Analytical Reagents*). Shorter monographs, such as those published by the G. Frederick Smith Chemical Company, or by Hopkin and Williams Ltd., of London, also contain much useful information pertaining to the field. Review articles describing the various aspects of the use of organic reagents are numerous, and the more comprehensive textbooks of analytical chemistry now devote considerable space to the discussion of organic reagents.

The writer has hesitated in making an excursion into a field so well documented. It has been pointed out, however, that a real need exists for a book dealing exclusively with the use of organic reagents in gravimetric and volumetric analysis. The use of organic reagents in colorimetric analysis, spot tests, etc., would not be treated, there being adequate coverage of these subjects in works by Sandell (*Colorimetric Determination of Traces of Metals*), Feigl (*vide supra*), and others. The function of this volume then is to describe the various organic reagents (precipitants) used in gravimetric and volumetric analysis; to indicate the type of analysis in which they may be used; and to provide proved directions for their use.

As to the contents: The material is presented in two sections, one devoted to theory and one to applications. This is an obvious, though convenient, division—one which permits a certain amount of emphasis on fundamental similarities among the various reagents.

In the theoretical section an effort is made first to give a condensed picture of the organic chemistry involved in the use of organic reagents. Similar material is presented in much greater detail by Feigl, Yoe and Sarver, and others; only the fundamentals are considered here. Next, the physical and chemical properties of the compounds with which the analyst deals are considered. Particular attention is paid to those properties which are important in analytical work. A general review of the theoretical section reveals the dearth of really fundamental information regarding the chelate complexes and their use in analysis, and should suggest courses for further research. The section concludes with a chapter devoted to special techniques that are required in analysis with organic reagents.

The second section contains chapters devoted to a detailed discussion of various organic precipitants. All the well-known reagents that are used in gravimetric and volumetric analysis are included, as well as numerous reagents of as yet minor importance. Some reagents are discussed in great detail, as a voluminous literature pertaining to their use testifies to their importance. 8-Hydroxyquinoline is one of these. Others, such as thionalide, are relatively new but very promising, and the details of their use are given in the hope of stimulating research on further applications. It will be noted that most of the reagents are of the type that form chelate complexes. This class has been thoroughly studied, and seems to offer much in the way of general applicability. Such reagents are reasonably selective if not specific, and their compounds have desirable properties from the analytical standpoint. It is not intended to imply, by this selection, a secondary importance for the so-called penetration compounds. These have also received much study, but show few if any advantages over reagents of the former type. The use of organic solvents in gravimetric analysis was considered outside the scope of this book.

The chapters dealing with the individual reagents are designed to afford as complete a picture as possible of the behavior of the reagent: how it reacts with the various ions, what properties its complexes have, and in what types of analysis it may be employed to best advantage. This has entailed a critical selection of methods which has, to a degree, been arbitrary. For a particular reagent, the methods for determining single elements in relatively simple mixtures are given. These are followed in many cases by methods for the analysis of some particular substance, such as an ore or alloy. These special methods have been included more to denote the scope of the reagent than to provide a compendium of analytical procedures, although naturally it is hoped that the methods given will prove to have practical value. The selection of these special methods was probably not unprejudiced. The book is written from the chemist's viewpoint, which frequently fails to consider the analytical problems of the biochemists, the metallurgists, and others. Nevertheless, the aim throughout is to present a sufficiently complete picture of the behavior of any reagent to enable the analyst in any field to adapt it to his problems.

Many of the methods given have been tested in the author's laboratory. Information regarding the accuracy and precision of methods is given wherever available. Other factors being equal, strong reliance has been placed on methods published by the National Bureau of Standards, and by the American Society for Testing Materials. Omitting the details of a particular method need not necessarily imply that the method is unreliable; it is hoped, however, that the methods given in detail include only reliable ones.

The book deals mainly with analysis on the macro scale; details of many micro methods have been omitted. For those interested, a reasonably complete bibliography of micro methods is included with each chapter.

The author has endeavored to make the bibliography complete and current, although he may have failed in some instances because of poor distribution of information during the past few years, or lack of close perusal of articles in fields not closely allied with chemistry. Survey of the literature has extended to early 1946. In the matter of the bibliography, the aid rendered by the Yoe and Sarver book, as well as the Hopkin and Williams Ltd. monograph, is freely acknowledged. The saving in time made possible by the use of their bibliographies was indeed great.

In glancing over the references included with each chapter, one cannot fail to be impressed by the large number of papers of Russian and German origin. The field of organic reagents, it would seem, has

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elicited high interest from the analytical chemists of these countries. It is hoped that American interest and research will keep pace.

Of the numerous contributions to the preparation of this book the author wishes to acknowledge particularly those of Dr. I. M. Kolthoff and Dr. M. L. Huggins in making suggestions concerning some of the chapters; of various individuals and agencies for granting permission to quote from their publications; of his wife, Clarice B. Flagg, for help in preparing the indices; of Mrs. Dorothy C. McCarty for proofreading and checking of material; and of Mrs. June P. Kern for typing the manuscript.

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GENERAL DISCUSSION

CHAPTER I

Organic Compounds as Precipitants for Inorganic Ions

Many varieties of organic compound have found application in analytical chemistry. These have been classified[1] broadly as solvents and wash liquids, substances used in neutralizations, organic oxidizing and reducing agents, indicators, primary standards, acidic and basic salt-forming compounds, photometric aids and substances used for the control of adsorption, diazotizing and coupling agents, and alkaloids and natural products. Of these compounds, however, those such as the indicators and primary standards are scarcely thought of as organic reagents in the sense that an organic reagent is a compound used for the detection or determination of organic or inorganic substances, and that a direct interaction between reagent and substance being determined usually occurs. The field is narrowed still more when we choose to consider only the acidic and basic salt-forming compounds and, indeed, this group will be considered only in part, for interest will center in those compounds forming salts that have been used successfully in gravimetric and volumetric inorganic analyses. This means that practically all compounds save those that form insoluble organometallic salts are excluded from consideration, and again interest must be confined to those of proven usefulness.

Included in the group of compounds to be considered are substances differing widely in constitution and mode of action, yet possessing the common property of forming insoluble organometallic salts under certain well-defined conditions. Some of these reagents form what might be considered "normal" (electrovalent) salts, and others, predominately covalent salts of the so-called inner-complex or chelate type. Still others combine with the inorganic substance in some obscure fashion, perhaps through a process involving adsorption. The chemical nature of the organic reagent is important in determining the type of

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[1] According to the usage of J. H. Yoe and L. A. Sarver, *Organic Analytical Reagents*. Wiley, New York, 1941.

salt to be formed. In this chapter the unique features of some organic compounds that make them "organic reagents" in the sense used here will be pointed out, and from a study of these features, which usually take the form of certain reactive groups within the molecule, further advances in the architecture of organic reagents should come.

For combination between an inorganic substance and an organic reagent to occur, the need for an affinity might be thought of which, in the ideal case, is so highly selective that only a single substance (ion) reacts. This ideal is never attained, and the analyst compromises on selective, rather than specific, action.

Specific reagents (or reactions) are those which, under the experimental conditions used, are indicative of one substance (or ion) only. Selective reagents (or reactions) are those which, under the conditions used, are characteristic of a comparatively small number of substances (or ions).

One aim of research in this field is the discovery of compounds possessing a high degree of selectivity; another is the discovery of the causes underlying such selectivity.

While most organic precipitants are selective only, various means are known whereby the selectivity of a reagent may be improved. These include adjustment of the *p*H, and the use of agents which form complexes with the elements, which, otherwise, might interfere with the determination. The tartrates and cyanides are typical complex-forming agents; numerous examples of their use will be found throughout the second section of this book. The function of *p*H in making a reagent more selective is discussed in detail in Chapter III.

Within the organic molecule there is generally a single acidic or basic group, or a combination of these, that is the key to the reactions of the compound. Such groups include the hydroxyl group in its various combinations (as hydroxyl, carboxyl, arsonate, etc.), the amino group or other groups containing basic nitrogen, the carbonyl group, the sulfhydryl group, and many others. In cases in which the precipitation occurs through an adsorption process, the precipitant usually contains large numbers of hydroxyl or carboxyl groups. In these instances a less well-defined compound may be formed than when simpler organic molecules are used.

The following sections of this chapter are devoted to a discussion of the various types of organic precipitants, with special emphasis upon the groups within the molecule that are responsible for the selective action. The salt-forming reagents and their reactive groups will be considered in some detail first, to be followed by a short description of the so-called adsorption precipitants and their mode of action.

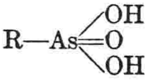
I. Salt-Forming Reagents

A. PRECIPITATION OF NORMAL SALTS

A number of organic compounds form normal salts (with inorganic ions) of sufficient insolubility to make them valuable as organic precipitants. Such compounds may be of an entirely acidic or basic character, as contrasted with compounds to be considered later that show both acidic and basic functions. The acidic reagents, such as oxalic acid, the arsonic acids, picrolonic acid, and hexanitrodiphenylamine (dipicrylamine), may be selective under a given set of conditions only, or not at all. Thus, the arsonic acids are selective precipitants for zirconium in strongly acid solution, but at high *p*H they will precipitate many cations. Oxalic acid, on the other hand, exhibits scarcely any selective action, regardless of *p*H. The precipitants that are bases generally lack selectivity; among these are compounds like benzidine, nitron, and the tetraphenylarsonium compounds.

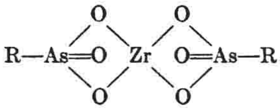
The following examples are chosen to indicate the type of salt formed in precipitations with this sort of reagent.

1. The Arsonic Acids,



$\mathrm{R{-}As(OH)({=}O)(OH)}$

These compounds combine with and precipitate the quadrivalent metallic elements in the fourth periodic group. The reaction occurs in rather strongly acidic solution The arsonic acids themselves are weak dibasic acids, one or both hydrogen atoms of which would possibly be replaced in forming salts (I). Two moles of reagent combine with one mole of a metal such as zirconium; the salt may contain the tetrapositive ion, or an oxygenated ion such as ZrO(II) (see also p. 108). The metallic arsonates are unsuitable for use as weighing forms, more perhaps because of difficulty in drying than because of uncertain composition.



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