

# ORGANIC FUNCTIONAL GROUP ANALYSIS

by

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## PREFACE

THE purpose of this book is to provide analytical chemists with a collection of versatile and reliable chemical methods for determining most of the more common organic functional groups. An attempt has been made to present the minimum number of methods required to solve the maximum number of problems. The scope and known limitations of each method are discussed so that the analytical chemist can decide whether the method under consideration can be applied to his particular problem. The actual procedures are written in such a fashion that they can be followed by competent non-technical personnel. Practically all of the methods discussed are in routine use in the various laboratories of Union Carbide Chemicals Company and I am grateful to this company for their cooperation in this project. I am also grateful to J. B. Johnson and J. E. Ruch for their helpful suggestions and excellent methods they have contributed to the field. Many other analytical chemists at Union Carbide have either contributed original procedures or valuable modifications that are presented. Where possible, these contributions are referenced. I am also indebted to R. S. Clark for technically editing the manuscript.

F. E. CRITCHFIELD





## CHAPTER 1

# INTRODUCTION

NEW techniques of organic analysis are being developed at a rate that is at least equivalent to the rate of expansion of the field of organic chemistry itself. One reason for this is the major role analytical chemistry plays in the rapidly expanding organic chemical industry.

This book is devoted to one aspect of organic analysis that is sometimes overlooked for the more glamorous instrumental techniques that are appearing upon the analytical scene. Chemical methods involve the determination of organic compounds via reactions of their functional groups and are usually simple, accurate, and precise means of analysis. This is not meant to imply that such chemical methods are analytical panaceas, because there are many analyses that can not be performed in this manner. In particular, chemical methods are of little value for analyzing hydrocarbons, ethers, and mixtures of compounds of the same homologous series. Such analyses can be more readily performed by instrumental methods, such as gas chromatography.

Chemical methods are particularly valuable for (1) the determination of the purity of refined materials; (2) the determination of ppm concentrations of organic compounds; (3) the analysis of research samples; (4) the calibration of instrumental methods; and (5) the rapid analysis of process samples.

This book contains a discussion of chemical methods recommended for determination of most of the more common organic functional groups. The principle, procedure, and scope and limitations of each method is discussed in detail. Practically all of the methods have been used routinely in the various laboratories of Union Carbide Chemicals Company and several of them have never been published heretofore.

No attempt has been made to provide a literature survey of methods for determining each functional group; however, references pertinent to the methods discussed are given. The particular methods selected for presentation in this book were selected mainly on the basis of general applicability, accuracy, reproducibility, and simplicity. A few methods of fairly limited applicability are discussed; however, in most of these cases the methods are presented because of their specificity. Some excellent chemical methods for organic functional groups may have been omitted; however, an attempt has been made to include those that fulfill the requirements specified above.

## TECHNIQUES

The techniques used in performing the methods discussed in this book are simple, and usually special equipment is not required for the analysis. The methods are either titrimetric or colorimetric in nature. The titrimetric methods are of most value for determining macro concentrations of organic compounds, while the colorimetric methods are recommended for determinations in the ppm range. Indicators are specified for selecting the end point of practically all titrations; however, in a few cases potentiometric titrations may be desirable and this will require the use of conventional pH meters. The colorimetric methods, of course, require a visible spectrophotometer.

Most of the reactions are conducted at room temperature or at the temperature of boiling water. In the latter case, the reactions are conducted in heat-resistant pressure bottles, enclosed in fabric bags, and immersed in a steam bath.

The use of pressure bottles for conducting reactions at elevated temperatures is very convenient and less subject to atmospheric contamination than reflux techniques. Some investigators may have misgivings about this application; however, the use of the bottles under the conditions specified is a safe operation. The particular bottles used in the author's laboratory\* have been

\* One source of supply for suitable bottles is B. Preiser Company Inc., Charleston, West Virginia. A source of supply for the fabric bags is Flaherty-Kennedy Filter Fabrics, Maplewood, New Jersey.

thoroughly safety tested at Union Carbide and no failures have been observed at pressures below 120 psig. Most of the bottles are capable of withstanding pressures up to 450 psig. Under the reaction conditions specified in the methods in this book, pressures higher than approximately 50 psig are not encountered.

## CHAPTER 2

# ACIDS AND BASES

A KNOWLEDGE of acid-base behavior in solution is essential to the understanding and application of organic functional group methods of analysis.

Several classes of organic compounds are sufficiently acidic or basic, under certain conditions, to be determined by direct titration with a basic or acidic titrant. A few of the compounds that can be determined directly in this manner are amines, amides, quaternary ammonium hydroxides, carboxylic acids, enols, phenols, and the acidic esters of sulfuric and phosphoric acids

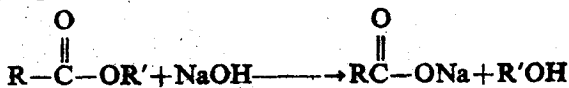
In addition to the acidic and basic substances, many compounds that are too weakly acidic or basic to be titrated directly can be reacted with a reagent to produce a measurable change in the acid-base characteristics of the system. In this indirect approach, the change can involve an acidic or basic reagent, or the formation of an acidic or basic product of the reaction. Examples of the indirect acid-base methods are:

### 1. Reaction with acidic or basic reagents

#### (a) Determination of epoxides



#### (b) Saponification of esters



### 2. Formation of acidic or basic products

#### (a) Acetylation of alcohols



## (b) Hydrolysis of imines



The changes in acid-base characteristics illustrated by these examples can be measured by acidic or basic titrants and, therefore, the reacting compounds themselves can be determined indirectly by an acid-base method.

Because of the large number of organic compounds that can be determined by acid-base methods, a discussion of some of the more important acid-base principles will be given in this chapter. In addition, methods used for the direct titration of acidic and basic substances will be discussed. Many of these direct acid-base procedures are also valuable as end-determinations in the indirect acid-base methods as will be observed in subsequent chapters of this book.

## SELECTION OF ACID-BASE METHOD

The selection of the best acid-base method for a particular purpose will depend upon several factors. If the compound to be determined is sufficiently acidic or basic to be titrated directly the following factors must be taken into consideration:

1. The acid-base strength of the compound,
2. The solubility of the compound and its salts in various solvents,
3. The presence of other acidic or basic substances in the sample.

The acid-base strength of the compound to be titrated will predominantly govern the solvent system selected for the titration. If the substance is a weak base, such as aniline, then an acidic solvent, like acetic acid, is desirable in order to enhance the basicity to a point that the titration is feasible. On the other hand, if the substance is an aliphatic amine, like ethylamine, the base strength is such that a wider choice of solvents is available.

Titration of the aliphatic amines can be performed satisfactorily in neutral solvents, water, slightly basic solvents and acidic solvents. The actual choice of the solvent in this case will be go-

verned by other factors, i.e. solubilities and the presence of interferences.

Similar considerations must be given to the selection of the correct solvent for the titration of acidic compounds.

Most carboxylic acids are sufficiently acidic so that they can be titrated satisfactorily in a wide variety of solvents including water, basic, neutral, and slightly acidic materials. However, basic media, such as pyridine, are usually required for the weaker aromatic hydroxylic acids, like phenol.

### *Relative Acidities*

The prediction of the relative strengths of acids and bases in nonaqueous media from their dissociation constants in water is not always possible, because structural effects may occur to a greater or lesser degree in nonaqueous media than in water. However, such predictions can be very useful as first approximations provided that their limitations are understood.

The relative acidities of a wide variety of organic acids have been studied in pyridine medium and compared with the corresponding acidities in water <sup>(12,14)</sup>. In general, accurate predictions can be made as to the relative acidities in pyridine, provided that the dissociation constants in water are known and the structures of the acids are taken into consideration.

Acidity studies in pyridine medium have been made by potentiometric titration of the acids with tetrabutylammonium hydroxide. Measurements of the acidity of acids in this medium are compared with the half-neutralization potential, *HNP*, of benzoic acid, which is arbitrarily assigned a value of zero. This technique is used to eliminate day to day variations in liquid-junction potentials.

When the acidities in pyridine, relative to benzoic acid, are compared to the dissociation constants in water, most monofunctional acids fall on one of the three curves in Fig. 1.

The three categories of acids that are described by Fig. 1 are:

- (1) The *ortho*-substituted benzoic acids (Curve 1),
- (2) Monocarboxylic acids and the *meta*- and *para*-substituted benzoic acids (Curve 2),

(3) *Ortho*, *meta*, or *para*-substituted phenols (Curve 3).

Within any of these three categories of acids, the acidities in pyridine relative to that in water remain constant. For example, acetic acid and *p*-nitrobenzoic acids have  $pK_a$ 's in water of 4.70 and 3.42 respectively. Reference to Curve 2 in Fig. 1 shows that the *HNP* of acetic acid in pyridine would be approximately 80 mv while the corresponding value for *p*-nitrobenzoic acid would be 110 mv. Thus, in water as in pyridine, *p*-nitrobenzoic acid is the stronger acid.

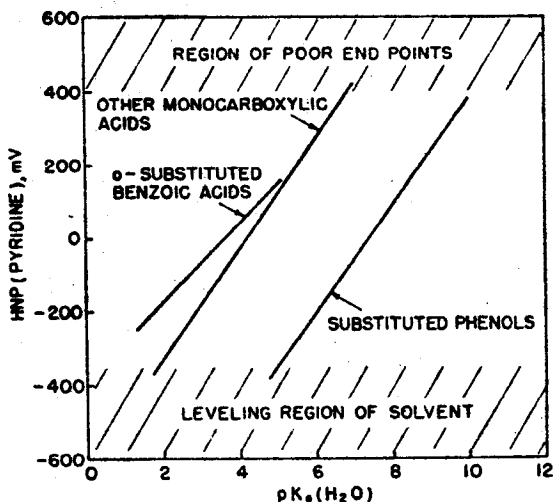


FIG. 1. Relative acidities in pyridine and water

The influence of the structure of acids on their relative acidities is illustrated by comparing the acidities of *p*-nitrobenzoic and *o*-chlorobenzoic acids in water and pyridine. The  $pK_a$  of *p*-nitrobenzoic acid is 3.42, as previously mentioned, while the  $pK_a$  of *o*-chlorobenzoic acid is 2.94. Thus, in water, the latter acid is the stronger. The *HNP* of *p*-nitrobenzoic acid in pyridine is 110 mv, while reference to Curve 1 shows the *HNP* of *o*-chlorobenzoic acid to be 75 mv. In pyridine medium, therefore, inversion of acidities occur, and *p*-nitrobenzoic acid is the stronger acid.

Comparative acidity studies such as this are invaluable to the selection of conditions for the titration of acidic substances.

The pyridine information is particularly valuable since pyridine is an excellent medium for the titration of acids.

From a knowledge of the dissociation constant of an acid in water and by reference to Fig. 1, it is possible to determine whether pyridine would be a satisfactory medium for the titration of acids that fall within the structural types listed.

Most *o*-, *m*-, and *p*-substituted benzoic and monocarboxylic acids are sufficiently strong in pyridine medium to be within the useful potential range of the solvent as illustrated by Fig. 1. However, Curve 2 shows that a hypothetical monocarboxylic acid or *m*-, or *p*-substituted benzoic acid with a  $pK_a$  in water of 7 would be too weakly acidic in pyridine to give sharp end points.

With substituted phenols, acids with  $pK_a$ 's less than 9.5 will give relatively sharp potentiometric breaks. Phenols with  $pK_a$ 's greater than 10 are too weakly acidic in this medium, and can be more successfully titrated in a more basic solvent such as ethylenediamine.

The effect of the aqueous dissociation constant on the sharpness of the potentiometric break in pyridine is illustrated by the curves in Fig. 2 for *p*-methoxyphenol,  $pK_a = 10.16$ ; and *m*-nitrophenol,  $pK_a = 8.35$ .

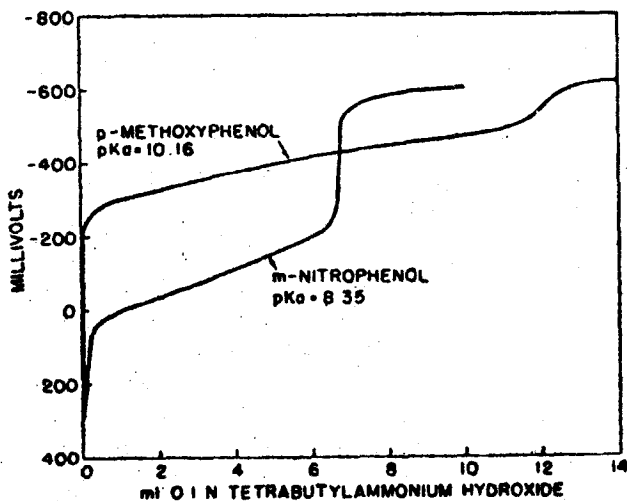


FIG. 2. Potentiometric titration of acids in pyridine



### Relative Basicities

The first study of relative basicities in nonaqueous media was performed in glacial acetic acid using perchloric acid as titrant for obtaining the neutralization curves<sup>(7)</sup>. In this study the absolute potential at the half-neutralization point *HNP* was taken as a measure of the basicity of the amines studied. The curve in Fig. 3 is a plot of *HNP* vs. the  $pK_a$  of the amines in water. The basicity of compounds in acetic acid medium is a linear function of the corresponding  $pK_a$ 's in water for compounds with  $pK_a$  (water) less than 4.0 (*p*-bromoaniline = 3.91). With compounds of greater base strength in water than pyridine ( $pK_a = 5.21$ ), the basicities in acetic acid medium are the same because these bases are ionized to such a large extent in the acidic medium. The leveling of acid-base strengths by the solvent is usually referred to as the leveling effect.

Glacial acetic acid is an excellent solvent for determining total basicities because of the leveling effect. However, the medium is not particularly useful for distinguishing between different basic species because of this effect. The medium can be used satisfactorily for the titration of bases with  $pK_a$  (water) greater than approximately 2.3. As indicated in Fig. 3 the potentiometric titration of weaker bases gives poorly defined end points.

Data on relative basicities in several non-protolytic solvents are available. In each of these cases the relative basicities

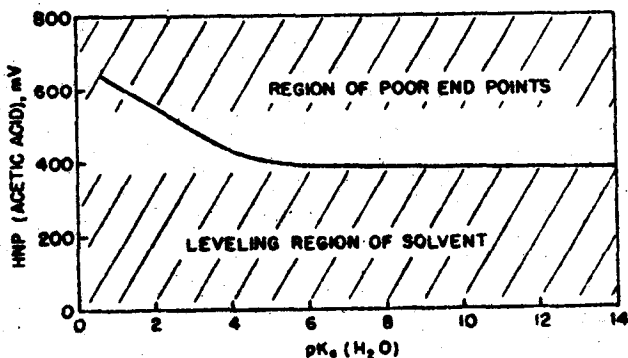


FIG. 3. Relative basicities in acetic acid