Epoxy Resins
Chemistry and Technology

Second Edition, Revised and Expanded

edited by

Clayton A. May

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Preface

The objectives of the second edition of this book have not changed substantially from those of the first. This volume is aimed at providing up-to-date assistance to the many who use, formulate, and synthesize epoxy resins. The revised and added chapters that follow contain information that will be of value to all who are involved with these materials. These range from the chemists and physicists faced with the problems of synthesis, chemistry, formulation, and processing of current and new products to the engineers who use epoxies to solve a complexity of hardware problems. To those who are newcomers to the field, this treatise provides a starting point which will bring them a step closer to the expert. To the expert it will be a profitable guide and reference source. The contents of these pages should prove invaluable to anyone who becomes or is involved with this complex area of materials technology and applications.

The second edition continues with a high degree of chemical orientation. The successful application of epoxy resins requires some fundamental understanding of the almost infinite combinations of resin and curing agent. Despite its size, this book is by no means a complete treatise on epoxy resins. To achieve this would have required an even greater number of pages. The contributors, however, have been selected with considerable care so that the text will be of value to a broad and varied audience. It is my hope and objective that the efforts of the contributors will help stimulate and guide the readers toward greater creativity in their particular field of endeavor.

The polymer and resin chemists should find the first four chapters most useful. The currently available commercial products are well documented. Many of the rarer species of epoxides also appear in the text and appended bibliographies. These chapters also afford excellent coverage of the resin curing mechanisms and the many available curing agents and modifiers. Chapters 5 through 12 deal with the applied technologies involving these materials. In Chapters 5 and 6, dynamic approaches to the subject matter have been used in conjunction with the more conventional static tests. Physical chemists and rheologists should find these approaches attractive. Following Chapter 12 are two chapters on analysis, which should be of great importance to those involved with quality assurance. Substantial gains have been made since the first edition in the area of physicochemical QA methods (Chapter 14). We now have a much better understanding of the processing and required quality of purchased products. This is prerequisite to the mechanically sound hardware of the future.

Chapters 1–4 are prerequisites for those responsible for the applied or formulative side of epoxy resins. Chapters 5–12 subdivide the applications of epoxy resins into physical properties of the cured resin; elastomer modification of the resins; adhesives; coatings; electrical and electronic applications; fiber-reinforced composites; and the use of epoxy resins in stabilization of polymers, plasticizers, and textiles. Here the reader will find keys to the formulation of a wide variety of end-use products.

To those engaged in using epoxy resins for hardware fabrication, the chapters dealing with applications are of prime importance. They help the user better understand the problems and thinking of the chemists and formulators. Further, the engineer must recognize that hardware manufacture with epoxy resins is a chemical process. To this end, Chapter 14 should be of great value. It is the basis for the quality assurance of purchased resins and formulations. It is also a forerunner to scientific processing of thermoset resins, an area of considerable research in recent years. Engineers who must deal with aerospace, aircraft, appliance, automotive, construction, electronic, flooring, maintenance, marine, poly(vinyl chloride), textiles, tool and die making, and transportation applications and their requisite processing will find this section of the book a valuable aid for their particular end use.

Finally, a few words about toxicity, hazards, and safe handling. It is a subject of importance to all who use these materials. Chapter 15, which is essentially a replication from the first edition, should be read by all who use this text. Safety should be foremost in our minds when handling epoxy resins.

As editors of the first edition, Dr. Yoshio Tanaka and I were fortunate in obtaining an outstanding group of international contributors to this field. None of this international flavor has been lost in this second edition. It has, however, been supplemented as new contributors have been added.

Repetitions are not uncommon in multiauthored works. The editorial efforts have once again been aimed at avoiding this pitfall. With this risk in mind, the authors have been afforded the maximum possible latitude. Recurrences of fact can be found, but these remain in the interests of making a chapter more useful and more easily understood. Every effort was made to give this panel of experts no more than guidelines, seeking their knowledge rather than that of the editor. Further, the book has been thoroughly indexed by the editor to assist the reader in finding all the information on a given subject.

My gratitude is expressed to all the contributors for their forebearance with our linguistic quibblings and their patience in smoothing out difficulties, obscurities, and differences of opinion. It is my sincere hope that our combined efforts have achieved a fair degree of clarity for a very complicated subject.

Clayton A. May

Contents

1

Introduction to Epoxy Resins

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I. INTRODUCTION

Since their conception, epoxy resins have been the subject of a multitude of patents and technical publications. Undoubtedly, there has been more written about these products per pound of sales than any of the other commercially available thermosetting resins. This immediately compels us to pose the question, why? In the chapters that follow, the answers become increasingly apparent.

This broad interest in epoxy resins originates from the extremely wide variety of chemical reactions and materials that can be used for the curing and the many different properties that result. The chemistry is unique among the thermosetting resins. In contrast to the formaldehyde resins, no volatiles are given off during the cure. This means that minimum pressures are required for the fabrication techniques normally used on these materials. The shrinkage is much less than that encountered in the vinyl polymerizations used to cure unsaturated polyester resins. This means reduced stresses in the cured product. Furthermore, a knowledge of the chemistry involved permits the user to cure over a wide range of temperatures and to control the degree of crosslinking. The latter plays an important role in the physical properties.

Considering the range of attainable properties, the versatility of epoxy resins becomes even more apparent. Depending on the chemical structure of the curing agent and the curing conditions, it is possible to obtain toughness, chemical resistance, mechanical properties ranging from extreme flexibility to high strength and hardness, high adhesive strength, good heat resistance, and high electrical resistance. Uncured, the resins have a variety of physical forms, ranging from low-viscosity liquids to tack-free solids, that, along with the curing agents, afford the fabricator a wide range of processing conditions. As a result of this versatility, these products have found use in protective coatings, adhesives for most substrates, body solders and caulking compounds, flooring, tooling compounds for molds, low-pressure molding resins, textiles, and fiber reinforced plastics. In the absence of curing agents, the epoxies are also useful as plasticizers and stabilizers for vinyl resins.

Since this book was originally published in 1973, numerous changes have occurred both in the chemistry and application of epoxy resins. Perhaps the most significant has been the intense interest in the use of these resins as the matrices for fiber reinforced plastics (FRP) or composites. The cause of this interest has stemmed primarily from two events. The first was the commercial availability of new fiber forms. Most important among these were the polyaramid or polyaromatic nylons (KEVLAR) and graphite or carbon fibers produced by the pyrolysis of rayon or polyacrylonitrile. The second important event was a developing awareness for the utility of FRP in aircraft and aerospace structures. Much of the credit for the latter belongs to the various Department of Defense (DoD) agencies and NASA. Now in use are both Air Force and Navy aircraft that contain well in excess of 1000 pounds of FRP per aircraft. The civil aircraft fields are close behind. An "all graphite/epoxy composite aircraft will shortly be available in the marketplace, and the Boeing Airplane Company is using substantial quantities of composite structure on the 757/67 series aircraft. More recently, the value of FRP to the automotive field has become increasingly apparent. Once this latter application reaches the production stage, not only epoxies, but the entire reinforced plastics and adhesive bonding industries as well, will expand at a rapid rate.

This intensified activity in the composites field has resulted in secondary rewards. Because large structures are expensive and human lives are becoming involved, product quality assurance has gained in importance. When the first edition of this book was published, composite hardware fabrication and adhesive bonding were more an art than a science. The intervening years have seen the evolution of chemical and physical test procedures that can be used to assure proper starting formulations and to verify that these materials have been properly processed. Thus the manufacture of products based on epoxy resins is changing from an engineering-oriented data sheet approach to one recognizing that these are chemical processes which can be controlled using chemical technology.

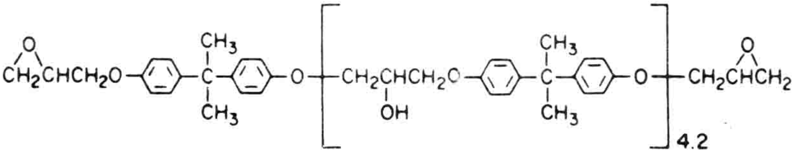
Another new area of development is the use of epoxy resins as chemical intermediates in the synthesis of other products of value in applications technology. The chapters on polymer stabilizers and textiles are cases in point. Further, although not discussed in this book, a variety of useful structural products can be manufactured from the "bis-GMA" resins. These latter materials, which are primarily the reaction products of various epoxy resins with the rapid cure technology of the unsaturated polyesters. Their main use is in conjunction with other vinyl monomers as the matrix resin for chemically resistant FRP structures. They are also the basis for a variety of commercial, fast-curing, plastic tooth filling compounds.

A growing need in recent years has been that of increased toughness. This is particularly true in the aerospace field as a composite matrix material. Simple plasticization will help to some extent, but only at the expense of valuable elevated temperature performance. The use of a second, discrete rubbery phase as a toughening agent is one approach toward this goal, which has minimal effect on elevated-temperature properties. In principle, it is of sufficient interest to form a new chapter (6) for this book. This is an area of continuing research, and, undoubtedly, other techniques of even greater significance will evolve in the years ahead.

II. HISTORY

A brief history of these products suffices because expanded reviews can be found in several earlier books on the subject.

Epoxy resins made their significant commercial debut around 1947. In the United States, the first product was made by the Devoe-Raynolds Company. It was essentially considered as a polyol for the preparation of synthetic drying oils and correspond to the approximate chemical structure:



(1)

At the end of World War II, the research vogue was synthetic drying oils made from the various fatty acids and resinous, polyfunctional alcohols. Functionality was a relatively new word, alkyd resins had become an important synthetic coating material, and the new approach was to place all of the hydroxyl functionality in a single molecule, such as shown in Structure 1.

Our laboratories (Shell Development) were busily engaged in this type of research. Shell Chemical Company became the first commercial producer of synthetic glycerin. Epichlorohydrin is an intermediate in the synthetic glycerol process and one of the key ingredients in the manufacture of epoxy resins. Thus the reaction products of epichlorohydrin with bisphenol A, when brought to our attention by Devoe-Raynolds, were of obvious interest. Through the properties of adhesion, toughness, and chemical resistance, epoxy resins of the structure shown (1) rapidly proved their value to the surface coatings industry. The use of epoxy resins as intermediates for protective coatings was the first major commercial application of this family of resins and still remains one of the most important.

Although 1947 marked the commercial debut of epoxy resins as we know them today, the true beginnings were much earlier. In 1909, the Russian chemist Prileschajew [1] discovered that olefins would react with peroxybenzoic acid to form epoxides. Peroxy acid epoxidations currently play an important role in epoxy resin production. In 1934, Schlack [2] of I. G.

Farbenindustrie AG in Germany applied for a patent on the preparation of high-molecular-weight polyamines by the reaction of amines with epoxide compounds containing more than one epoxide group. Among the various materials was a product prepared from epichlorohydrin and bisphenol A. It was disclosed that this resin could be hardened with equivalent amounts of amine. However, Schlack and/or I. G. Farben failed to recognize of the significance of the latter part of this invention.

The realization of the true value of these products came a few years later. Almost simultaneously and independently, two inventors, Pierre Castan in Switzerland and Sylvan Greenlee in the United States, recognized the value of epoxy resins as we know them today. Castan [3] was conducting research on new denture materials and in 1938 filled a patent that describes the preparation of the diglycidyl ether of bisphenol A from epichlorohydrin and bisphenol A. The Castan disclosure revealed that the resin, when cured with phthalic anhydride, had excellent adhesion to a variety of substances. It is interesting to note that Castan's dental application never attained commercial fruition, but the bis-GMA resins mentioned earlier are the primary materials in tooth filling applications. Commercial epoxy resin production today utilizes preparative procedures similar to those of Castan. However, most of the lower-molecular-weight epoxy resins are now made by a continuous process.

The approach taken by Greenlee was different. His first patent, filled in 1943 [4], describes very similar resins made by the same process as Castan's but higher in molecular weight. Today many of the higher-molecular-weight resins are made by condensation of the diglycidyl ether of bisphenol A and bisphenol A. Greenlee's objective was primarily the preparation of a polyol for esterification with drying oil fatty acids to be used in surface coatings. It was this approach that led to successful commercialization in the United States.

During this same period, in the early 1940s, Daniel Swern was studying epoxidation by another route, the reaction between peroxy acids and olefins. Among his many publications is an excellent review on this subject [5]. The current commercial process, which is based on peroxyacetic acid, is used for the production of epoxidized drying oil plasticizer–stabilizers for vinyl chloride polymers and several cycloaliphatic epoxy resins. The peracid process is discussed in detail in Chapter 2, Section IV.C. Although not clearly delineated in the federal statistics, the epoxide resin plasticizer market is substantial. Sales of epoxidized oils are estimated to be well in excess of 100 million pounds annually [6].

III. COMMERCIAL GROWTH AND END-USE PATTERNS

The use of epoxy resins has grown steadily since their commercialization in the late 1940s. Data on their consumption from 1954 to date are shown in Figure 1. The early information was obtained from the U. S. Tariff Commission Reports [7] and more recently from *Modern Plastics* [8].

The data in Figure 1 show that the consumption of these products increased by about 20% per year until 1978. Since 1978, consumption has been fairly steady. This probably reflects the stagnation of business generally during this period. Increased consumption in the future is thus anticipated,

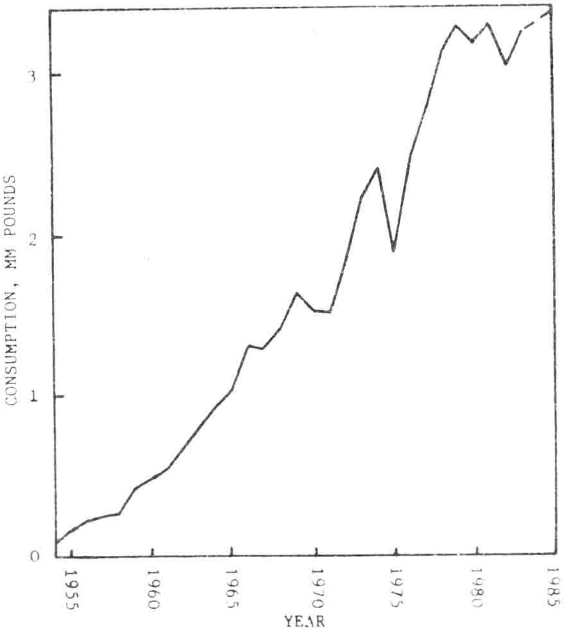


Figure 1. Consumption of bisphenol-type epoxy resins in the United States since 1954.

particularly in light of recent aerospace and automotive activities. Overall, although the growth of these materials has not been spectacular, it has been quite healthy. Undoubtedly, resin prices have been a major deterrent to more rapid acceptance. For example, the liquid diglycidyl ether of bisphenol A cost one dollar per pound as late as 1953. Subsequently the price declined steadily until around 1973 (80 cents in 1954, 65 cents in 1958, 56 cents in 1965 and 41 cents in 1973). Prices have subsequently risen to a current level (1986) of around $1.25 because of inflationary pressures and raw material costs. Their major competition, particularly in the structural fields, comes from the unsaturated polyester resins and phenolics. Thus the choice of an epoxy resin is a compromise of increased performance for a higher price.

The end use pattern of epoxy resin consumption covers a broad range of applications as cited earlier. Figure 2 shows the annual consumption of these materials subdivided into five categories: coatings, structural applications, bonding and adhesives, exports, and miscellaneous. Since their commercialization, surface coatings have remained the largest single application and account for around 40-45% of the annual sales. The recent spurt in the growth pattern has been in the field of structural applications which includes FRP hardware. Undoubtedly, aerospace applications of these materials is the underlying reason. Adhesives, which include flooring, paving, and aggregate materials, have also shown steady, but less spectacular growth.

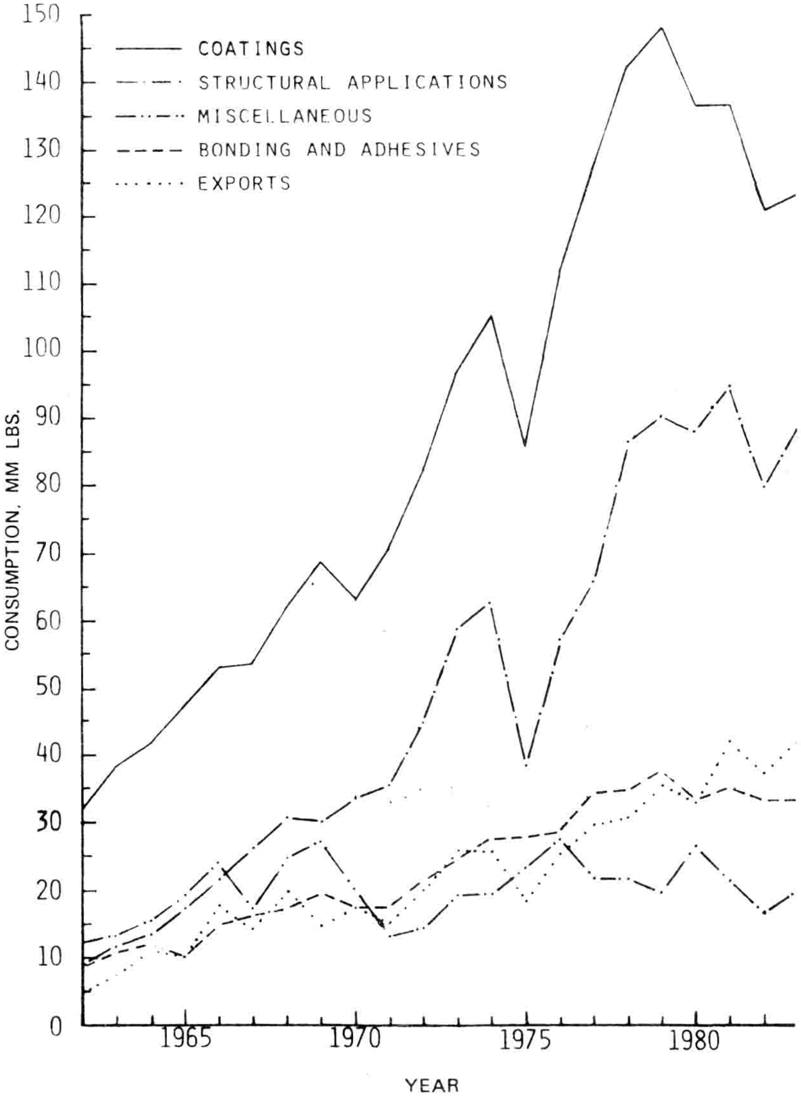


Figure 2. Pattern of epoxy resin consumption since 1962.

A more complete picture of epoxy resin consumption by end use is given for 1980 in Figure 3. The broad range of applications explains why these materials are discussed so widely in the technical literature. No single application exceeds 12% of the total consumption. If we compare these data with a similar analysis made 10 years ago, it is of interest to note that the percentage share of usage for structural applications has increased by around 20%, whereas the coating market continues at 40–45% of the total.

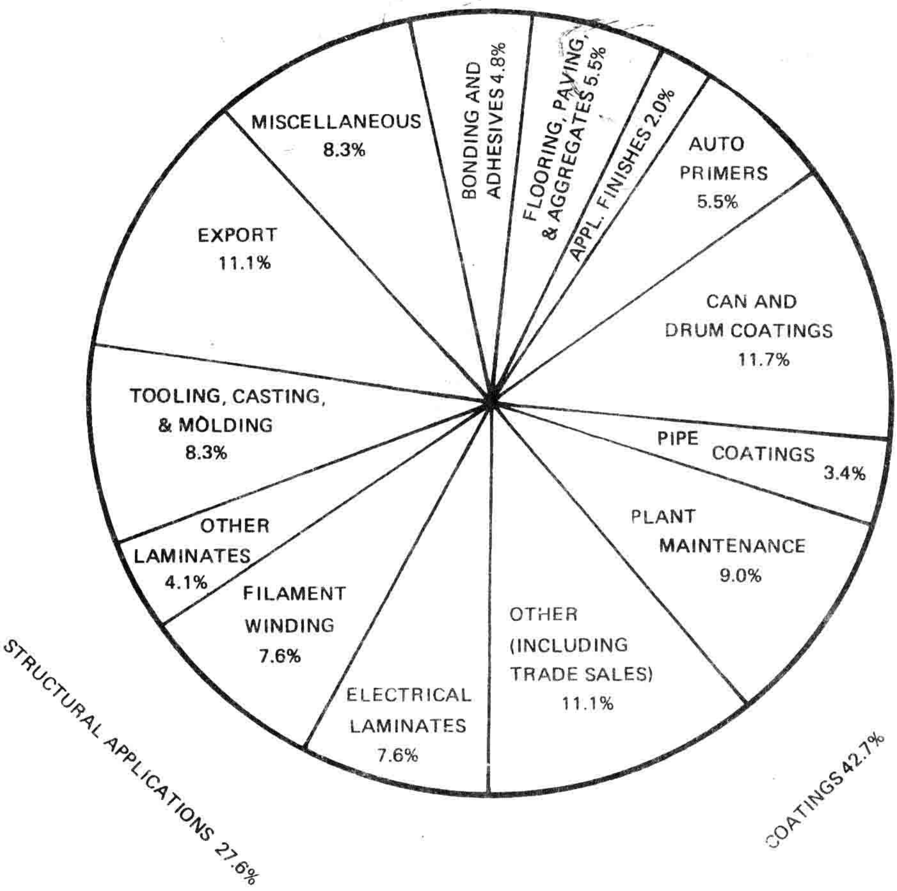


Figure 3. Epoxy consumption, by end uses.

It would thus appear that the highest future growth will be in the areas of structural applications, most probably for FRP hardware.

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2

Synthesis and Characteristics of Epoxides

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I. INTRODUCTION

The term *epoxy* is a prefix referring to a bridge consisting of an oxygen atom bonded to two other atoms already united in some way. This chapter deals only with the synthesis and characteristics of the three-membered ring α- or 1,2-epoxides wherein the other two atoms are carbon. The capability of this group to undergo a large variety of addition and polymerization reactions leads to the numerous thermoplastic and thermosetting forms of epoxy resins. We define an *epoxy resin* as any molecule containing one or more 1,2-epoxy groups. The chemistry of 1,2-epoxides has been reviewed by numerous authors, including Winstein and Henderson [1], Eliel [2], Parker and Isaacs [3], Rosovsky [4], Malinovskii [5], and Buchanan and Sable [6]. Reviews on epoxy resins have been published by Lee and Neville [7], Coderre [8], Skeist [9], Paquin [10], Harper [11], St. Pierre [12], Kastens [13], Wismer [14], Furukawa and Saegusa [15], Schrade [16], Landau and Lidov [17], Ishii and Sakai [18], Pruckmayr [19], May and Tanaka [20], and Sandler and Karo [21]. Some aspects of epoxide chemistry have also reviewed by Dittus [22], Staude and Patat [23], Schoenberg [24], Yandovskii and Ershov [25], Buddrus [26], Tomalia [27], Wohl [28], Lane [29], Meleshevich [30], Huisgen [31], Stirling [32], and other [33-46].

The nomenclature of epoxides is confusing [47]. In addition to the 1,2-epoxide, there are a large variety of heterocyclic compounds with similar-sounding names. The reader can thus easily go astray in searching the literature. To avoid this pitfall, we briefly point out some of the more misleading facets.

Monocyclic compounds containing more than one type of atom in a heterocyclic ring are named by combining a prefix that describes the additional element with a stem that describes the ring size and degree of unsaturation. The prefixes for the various elements in a hetero ring system are shown in Table 1, in which the "a" is elided where necessary. Table 2 lists the stems for the various oxygen and nitrogen saturated and unsaturated heterocycles in three- to ten-membered rings. Note the similarity between ethylene oxide, trimethylene oxide, and tetrahydrofuran, which are called oxirane, oxetane, and oxolane, respectively. A further point of confusion arises from the numerous epoxy prefixes, as shown in Table 3. In this system ethylene oxide is called epoxyethane.

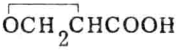
There are additional names for 1,2-epoxides that add further to the confusion. Cyclohexene oxide is variously referred to as 1,2-epoxycyclohexane, 1,2-oxidocyclohexane, and 7-oxabicyclo[4.1.0]heptane. When epoxides are regarded as derivatives of α-glycols, the prefix *anhydro* is used throughout the text in conjunction with the convenient *glycidyl*, which several of the simple epoxides have common names that tell little about their structure. 1-Chloro-2,3-epoxypropane (1), 1,2-epoxy-3-hydroxypropane (2), and 2,3-epoxypropanoic acid (3) are called epichlorohydrin, glycidol, and glycidic acid, respectively.

$\overline{OCH_2C}HCH_2Cl$

(1)

$\overline{OCH_2C}HCH_2OH$

(2)



$\overline{OCH_2C}HCOOH$

(3)

The terms *epoxy* and *epoxide* are most commonly used to describe the oxirane ring. The latter is doubtless more correct. The term *epoxide* is used throughout the text in conjunction with the convenient *glycidol*, which is used to describe the terminal epoxy group, $\overline{OCH_2C}HCH_2-$. The prefix is modified by "ether," "ester," "amine," etc., according to the group attached to the third carbon atom.

Because this chapter is concerned with recent developments in the synthesis of epoxides, reference is made only to investigations that appear to throw light on the epoxidation reactions involved. This selection is at times subjective, but we have tried to present all of the important evidence. In addition, a section on structure is included, because it is desirable to have structure clearly in mind in considering the characteristics of epoxides.

II. MOLECULAR AND ELECTRONIC STRUCTURES OF EPOXIDES

The bond lengths and angles in oxirane or ethylene oxide have been determined by electron diffraction [1,49] and by microwave spectroscopy [50, 51]. The bond angles of C–O–C, O–C–C, and H–C–H are 61°24', 59°18', and 116°15', respectively. The bond lengths are C–C = 1.47, O–C = 1.44, and C–H = 1.08 A, respectively. Each CH_2 group is in a plane at right angles to the plane of the ring, and the angle between each CH_2 plane and the C–C bond is 159°25'. Table 4 shows molecular structures of various heterocyclic compounds, including oxirane.

1,2-Epoxypropane, 1-chloro-2,3-epoxypropane, and the *cis*- and *trans*-2,3-epoxybutanes have been investigated by electron diffraction [1,49], and in each case the bond joining the exocyclic carbon atom to the ring is 1.52 ± 0.03 Å. The length of this bond in 1,2-epoxypropane or propylene oxide was found by microwave spectroscopy to be 1.51 ± 0.02 Å [53].

A microwave-spectroscopy study of 1,2-epoxycyclopentane has shown that the oxygen atom is outside the approximate plane of the carbon ring [54]. The carbon–carbon distance in the epoxy ring is 1.52 Å; the carbon–oxygen distance is 1.47 Å; and the angle between the carbon ring and the epoxy ring is 98.1°.

An electron-diffraction investigation of 1,2-epoxycyclohexane has shown that the four carbon atoms nearest to the oxygen are coplanar [55]. The angles $C_1-C_2-C_3$ and $C_2-C_1-C_6$ have been found to be 118.5°; the angles $C_2-C_3-C_4$ and $C_1-C_6-C_5$ are 116°, and the angles $C_3-C_4-C_5$ and $C_4-C_5-C_6$ are 109.5°. The bond lengths are, for C–C, 1.54 and for C–O, 1.42 Å.

Crystal and molecular structures of some epoxides, such as 1,2;3,4;5,6-triepoxycyclohexane [56], *anti*-2,3;4,5-diepoxy-12-oxa[4.4.3]propella-7,9-diene [66], and *anti*-2,3;4,5-*syn*-7,8;9,10-tetraepoxy-12-oxa[4.4.3]propellane [66], were investigated by x-ray analysis [56–67], and geometry of some epoxy rings was tabulated by Foces-Foces et al. [58] and Rodiou et al. [61]: The angles C–O–C and C–C–O have been found to be 59.5°–63.4° and 57.1°–60.8°, respectively. The bond lengths are C–O = 1.407–1.465 Å and C–C = 1.453–1.500 Å. These variations seem to show that the epoxy group follows a systematic deformation so as to keep the area of the ring constant, with variations in the angles C–C–O and C–O–C and in bond distances C–O and C–C [58].

Replacement of a CH_2 group in a cycloalkane by an oxygen atom introduces a dipole moment into the molecule. The dipole moment of oxirane is 1.82 D in benzene solution and 1.91 D in the gas phase [68]. The values for oxetane, tetrahydrofuran, and tetrahydropyran in benzene are reported as 1.92, 1.75, and 1.55 D, respectively [69].

Measurements of the heats of formation [70,71] and heats of combustion [72] of the simpler cyclic ethers indicate the considerable strain present in the three- and four-membered rings. The ethers and strain energies in kilojoules per mole are as follows: oxirane, 117.2, 114.1; oxetane, –, 106.7; oxolane, 28.0, 23.6; oxane, 9.2, 4.9. This results from the fact that a carbon-oxygen bond is shorter than a carbon-carbon bond, as indicated above.

The heat of mixing with chloroform, the frequency shift of the O–D band in the infrared spectrum of CH_3OD solutions [73,74], and the chemical shifts in proton magnetic resonance [75] show that the electron density on the oxygen atom is unusually low as compared with that in acyclic and large-ring cyclic ethers. The calculated charge distributions for a series of epoxides are shown in Table 5. The behavior of the ether is governed by the nature of the lone-pair electrons on the oxygen, because the lone-pair electrons form a basic site for the addition of acids such as protons and Lewis acids, and for the formation of oxonium salts. Therefore, the chemistry of cyclic ethers may depend largely on the nucleophilicity of the ether oxygen; the nucleophilicity varies with ring size and with substituents. This variation seems to result from changes in hybridization of the orbitals at the oxygen atom and from changes in steric hindrance toward electrophilic at-