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Chapter One

HOW TO USE INDUSTRIAL ORGANIC CHEMICALS, SECOND EDITION

Industrial Organic Chemicals, published in 1996, was an updated, expanded, and completely rewritten version of volume I of a two-volume set, *Industrial Organic Chemicals in Perspective*, published in 1980. Volume I of the set described where industrial organic chemicals came from; volume II described how they were used. Two decades later, chemicals still come from the same sources, but there are many new processes to be described. The application of chemicals has changed much less, and a revision of volume II is not planned. This second edition of the 1996 book is warranted by the numerous changes the industry has undergone in a short time. We discuss many new processes and improvements in many older ones.

0.1 WHY THIS BOOK WAS WRITTEN AND HOW IT IS STRUCTURED

The petrochemical industry provides well over 95% by tonnage of all organic chemicals. It grew rapidly in the 1950s and 1960s. Many new processes and products were introduced. Large economies of scale proved possible. The prices of chemicals and polymers dropped so that they could compete with traditional materials. Cheerfully colored plastic housewares, highly functional packaging, shampoos that tolerated hard water and easy care garments of synthetic fibers were no longer exciting new technology. Instead they had become an accepted and routine part of modern life.

By the 1970s, growth was leveling off. The first and second oil shocks increased the price of crude oil, and hence of its downstream products. Economies of scale suffered a hiatus to rise again in the late 1990s with the announcement of 2.2 billion lb of ethylene per year steam crackers and a 3.5 billion lb per year methanol plant. In 2004, SABIC announced plans for a 2.9 billion lb/year cracker. The industry had matured. As its technology became better known, developing countries started their own petrochemical industries, competing with the developed countries and thus depressing profitability. Furthermore, the impact of the industry on the environment became evident.

In the 1980s and early 1990s, new products were no longer the name of the game, in part because the 1960s and 1970s had provided an arsenal of them to attack new applications. Also, the industry became subject to strict government monitoring. Expensive toxicity testing was required before a new compound could be introduced. (Section 1.3.7).

Rather than developing bigger, better plants to manufacture novel chemicals, the industry became concerned with lessening pollution, improving processes, and developing specialty chemical formulations and niche products that could be sold at higher profit margins. Research and development became highly process oriented, in part to find less polluting processes, and in part to combat maturity and gain an edge over competition with money-saving technology. Examples are given in the foreword and throughout the book.

Chapter 1 shows how the chemical industry fits into the overall economy and then defines the industry in terms of its characteristics.

Chapter 2 describes where organic chemicals come from and then shows how the major sources, petroleum and natural gas, provide seven basic chemicals or chemical groups from which most petrochemicals are made. The basic building blocks comprise olefins-ethylene, propylene, and the [C.sub.4] olefins (butadiene, isobutene, 1- and 2-butenes); aromatics-benzene, toluene, and the xylenes (*ortho, meta, para*); and one alkane, methane. Chapter 2 explains how the olefins derive primarily from steam cracking and secondarily how [C.sub.3] and [C.sub.4] olefins come from catalytic cracking, and how the aromatics derive primarily from catalytic reforming in the United States but from steam cracking in Europe. Methane occurs as such in natural gas. The chapter emphasizes the important interface between the refinery and the petrochemical industry and the relationship between feedstock flexibility and profitability.

Chapters 3 and 4 describe the chemistry of ethylene and propylene. They are the most important of the seven building blocks and are treated accordingly.

Chapters 5 and 6 deal with the [C.sub.4] and [C.sub.5] olefins. Chemical usage of [C.sub.4] olefins (excluding methyl-*tert*-butyl ether for gasoline) is an order of magnitude less than that of ethylene and propylene, and the major [C.sub.4] applications are in synthetic rubbers. The [C.sub.5] compounds and their derivatives are only used in much lower volume and are not included in the seven basic building blocks. They are nonetheless an important source of isoprene for a synthetic analogue of natural rubber (Section 15.3.10) and for thermoplastic elastomers (Section 15.3.8).

Chapters 7-9 describe the chemistry of the aromatics-benzene, toluene, and the xylenes. Benzene has been overshadowed by ethylene

and propylene since the 1960s but is still the third most important of the building blocks.

Chapter 10 describes the chemistry of methane, a relatively unreactive molecule, which nonetheless is the source of synthesis gas (CO + [H.sub.2]) for ammonia and methanol manufacture. Acetylene is discussed here, since it may be made from methane. Very important 50 years ago, its significance has been steadily diminished by chemistry based on ethylene and propylene.

Chapter 11 is devoted to the growing industrial chemistry based on alkanes other than methane. The substitution of alkanes for olefins, which depends on sophisticated catalyst development, could change industrial chemistry profoundly in the future.

Chapters 12-14 deal with non-petroleum sources of chemicals-coal, fats and oils, and carbohydrates. The chemical industry in the nineteenth and early twentieth centuries was based on chemicals derived from coal tar or coke oven distillate. Today, this is a specialty area, and our major interest in coal focuses on its conversion to synthesis gas. This would be the first stage in building a coal-based chemical industry should petroleum and natural gas be depleted.

The chemistry of fats and oils (Chapter 13) is reflected in the surfactant area and in numerous specialty performance products. Carbohydrate-based chemicals (Chapter 14) are also largely specialties.

Since over one-half of all organic chemicals manufactured end up in polymers, Chapter 15 is devoted to polymerization processes and polymer properties. Chapter 16 deals with the all-important subject of catalysis without which there would hardly be a chemical industry. Chapter 17 discusses the vital issue of sustainability, and the emergence of "green" chemistry, a topic that dominates the books published on industrial chemistry since 1990.

It is these new processes and attitudes that provided the incentives for this new volume, but we have also expanded its scope to include many apparently less important reactions, which are significant because they give rise to the more profitable specialty chemicals. We hope it will be useful both to university students who have studied organic chemistry and to graduates and industrial chemists who work in or are interested in one of the most remarkable industries of the twentieth century and, if we may anticipate a little, the twenty-first century.

We intend each chapter to be self-sufficient, hence there is inevitably a degree of repetition. We have tried to minimize this by extensive cross-referencing and hope the reader will be tolerant of the repetition that remains.

0.2 NORTH AMERICAN INDUSTRY CLASSIFICATION

The US government provides statistics on all branches of industry, dividing them according to the North American Industry Classification System (NAICS). Each major segment of the economy is classified under a number between 1 and 99 (Table 1.1). Manufacturing industries are classified under numbers 31-33 and the chemical and allied products industry falls within this category at 325. Statistics for subsegments of the industry are provided under four, five, or six digit numbers. Thus 3252 is *Resins, synthetic rubbers & artificial & synthetic fibers and filaments*, 325211 is *Plastics materials and resins*, 325212 is *Synthetic rubber*, and 32522 *Artificial & synthetic fibers and filaments*. We have relied on these data, although it is never possible to obtain up-to-date figures. Thus the material published in 2002 contains information for 2000. Statistics from other sources are often more up-to-date but are less authoritative (Section 0.4.5).

The industries that form the chemical and allied products industries are shown in Table 1.2. Although at times one might wish for even more detailed information, the North American Industry Classification provides a wealth of it. Other countries do not have comparable databases; many have Standard Industrial Classifications, but none provides so much information. The classifications in other countries rarely correspond to those in the United States or to each other, and analysts wishing to tackle official statistics should be aware of the pitfalls.

0.3 UNITS AND NOMENCLATURE

The widespread adoption of the SI (SystÃ¨me International) system of units based on the meter, the kilogram, and the second has worsened rather than improved the plethora of units used in the chemical industry. Three kinds of tons are in common use-the short ton (2000 lb), the metric ton or tonne (1000 kg or 2204.5 lb), and the long ton (2240 lb). U.S. Statistics are usually given in millions of pounds, which are at least unambiguous, and we give all our figures either in these units or in tonnes. In addition, we try to quote figures in the units actually used by industry-petroleum is measured in barrels, benzene in gallons, mixed xylenes in gallons, and (incredibly) *p*-xylene in pounds-to give conversions in better known units. A table of conversion factors is given in Appendixes 2 and 3.

Similarly, in naming chemicals, we tend to use the names conventional in industry rather than the more academic nomenclature of the International Union of Pure and Applied Chemistry (IUPAC). Thus we write hydrogen not dihydrogen; ethylene, acetylene, and acetic acid; not ethene, ethyne, and ethanoic acid.

Industry makes no effort to use consistent nomenclature. Ethene and propene are universally known as ethylene and propylene and would scarcely be recognized by their IUPAC names. The [C.sub.4] olefins, however, are frequently referred to as butenes rather than butylenes and we have followed this style. We use trivial names wherever industry does. Thus we refer to [C.sub.6][H.sub.5]CH[(C[H.sub.3]).sub.2] as cumene, the name by which it is bought and sold, rather than the more informative names of isopropylbenzene, 2-phenylpropane, or (1-methylethyl)benzene. The term ethanal would be likely to be misread or misheard in industry as ethanol, and the compound is known as acetaldehyde. So important is trivial nomenclature that the pharmaceutical industry could not exist without it.

We regret the lack of consistency that the use of trivial nomenclature entails, but we feel it best serves our aim of communicating with

chemical industry personnel and preparing students to enter the industry.

0.4 GENERAL BIBLIOGRAPHY

In many ways, the greatest service that a book like this can provide is to introduce the student to the industrial chemical literature. We follow each chapter with an annotated bibliography that lists some of the standard literature on the subject of the chapter, cites the sources of much of our own information, and adds occasional notes to matters discussed in the chapter. Two of the authors of this book received their basic education many years ago, and we have listed unashamedly the books that influenced us, aged though they may be. We have omitted some of the truly obsolete material. References to early work, as well as more recent material, may be found in *Kirk-Othmer* and other encyclopedias, and in B. G. Reuben and M. L. Burstall, *The Chemical Economy*, Longman, London, 1974. Relatively few books have been written recently on the chemical industry and much can still be gained from the old ones.

0.4.1 Encyclopedias

The most important single reference work is R. E. Kirk and D. F. Othmer, *Kirk-Othmer's Encyclopedia of Chemical Technology*, Volumes 1-25, 4th ed., J. I. Kroschwitz and M. Howe-Grant, Ed., Interscience, New York, 1991-1998. *Kirk-Othmer* provides comprehensive and well-referenced coverage of almost every aspect of industrial chemistry. New articles appear on the web (www.mrw.interscience.wiley.com/uric or www. mrw.interscience.wiley.com/kirk) and these will eventually be included in a 5th edition. The earlier volumes of the first, second, and third editions are inevitably dated, but provide information not readily available from other sources. If a subject is not treated in the new edition, it is always worth consulting the older one.

The Encyclopedia of Polymer Science and Engineering, 2nd ed., J. I. Kroschwitz, Ed., (17 volumes plus supplement and an index volume) Interscience, New York, 1985-1989, provides comprehensive coverage of polymer chemistry. It is well referenced but weak on technology. The first edition (called *The Encyclopedia of Polymer Science and Technology*) comprised 15 volumes and was published between 1964 and 1971. As with *The Encyclopedia of Chemical Technology*, the earlier edition still contains valuable material. Part 1: Volumes 1-4 of the 3rd ed. (reverting to the original title, H. F. Mark, Ed.) had been published by June 2003.

The Encyclopedia of Chemical Processing and Design, J. J. McKetta, Ed., Dekker, New York, has a chemical engineering orientation. It had run to 68 volumes by 1999. As publication started in 1976, it is perhaps inevitable that the approach is inconsistent. Individual articles are worthwhile but the content is unpredictable.

The only encyclopedia to rival *Kirk-Othmer* is *Ullmann's Encyclopedia of Industrial Chemistry*, W. Gerhartz, Ed., Wiley-VCH, Weinheim. It was first published in 1914 and this, the 6th ed., appeared as a 40-volume set in October 2002. A rapid inspection suggests rigorous editorial control, with well-indexed chapters following a standard pattern. It has a more international approach than *Kirk-Othmer*.

An ambitious undertaking is the *Dictionary of Scientific and Technical Terms*, S. P. Parker, Ed. The 4th ed. was published by McGraw-Hill in 1989. Two newer ventures are R. D. Ashford, *Dictionary of Industrial Chemical Properties, Production and Uses*, 2nd ed., Wavelength, London, 2002, and A. Comyns, *Encyclopedic Dictionary of Named Processes in Chemical Technology*, CRC Press, Cleveland OH, 1999.

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Industrial Organic Chemistry, 5th Edition. Description. About the Author.Â It should appeal most to chemists and engineers in the chemical industry, who should benefit from the technological, scientific and economic interrelationships and their potential developments." (Synthesis - Journal of Synthetic Organic Chemistry). Where Is Organic Chemistry Used? Organic chemistry is a highly creative science in which chemists create new molecules and explore the properties of existing compounds. It is the most popular field of study for ACS chemists and Ph.D. chemists. Organic compounds are all around us. They are central to the economic growth of the United States in the rubber, plastics, fuel, pharmaceutical, cosmetics, detergent, coatings, dyestuff, and agrichemical industries, to name a few. Books.google.ru - A comprehensive overview of industrial organic chemicals The majority of industrial organic chemicals and polymers are derived from seven major building blocks produced from petroleum and natural gas. While the fundamentals of this technology have remained constant in recent decades, the organic chemical

Industry: 2869â€”Industrial Organic Chemicals, Not Elsewhere Classified. Establishments primarily engaged in manufacturing industrial organic chemicals, not elsewhere classified. Important products of this industry include: (1) aliphatic and other acyclic organic chemicals, such as ethylene, butylene, and butadiene; acetic Industrial Organic Chemicals SIC2869 MDocuments. SHELL CHEMICAL markets these ORGANIC CHEMICALSDocuments. Chemical Classification : Composition :Organic Chemicals / HydrocarbonsDocuments. GFS Chemicals Organic Chemical Product ListingDocuments. Synthetic Organic Chemicals for the Textile IndustryDocuments. From the Armour Chemical Division.ALIPHATIC ORGANIC CHEMICALSDocuments. Anand Chemicals, Hyderabad, Organic ChemicalsBusiness.