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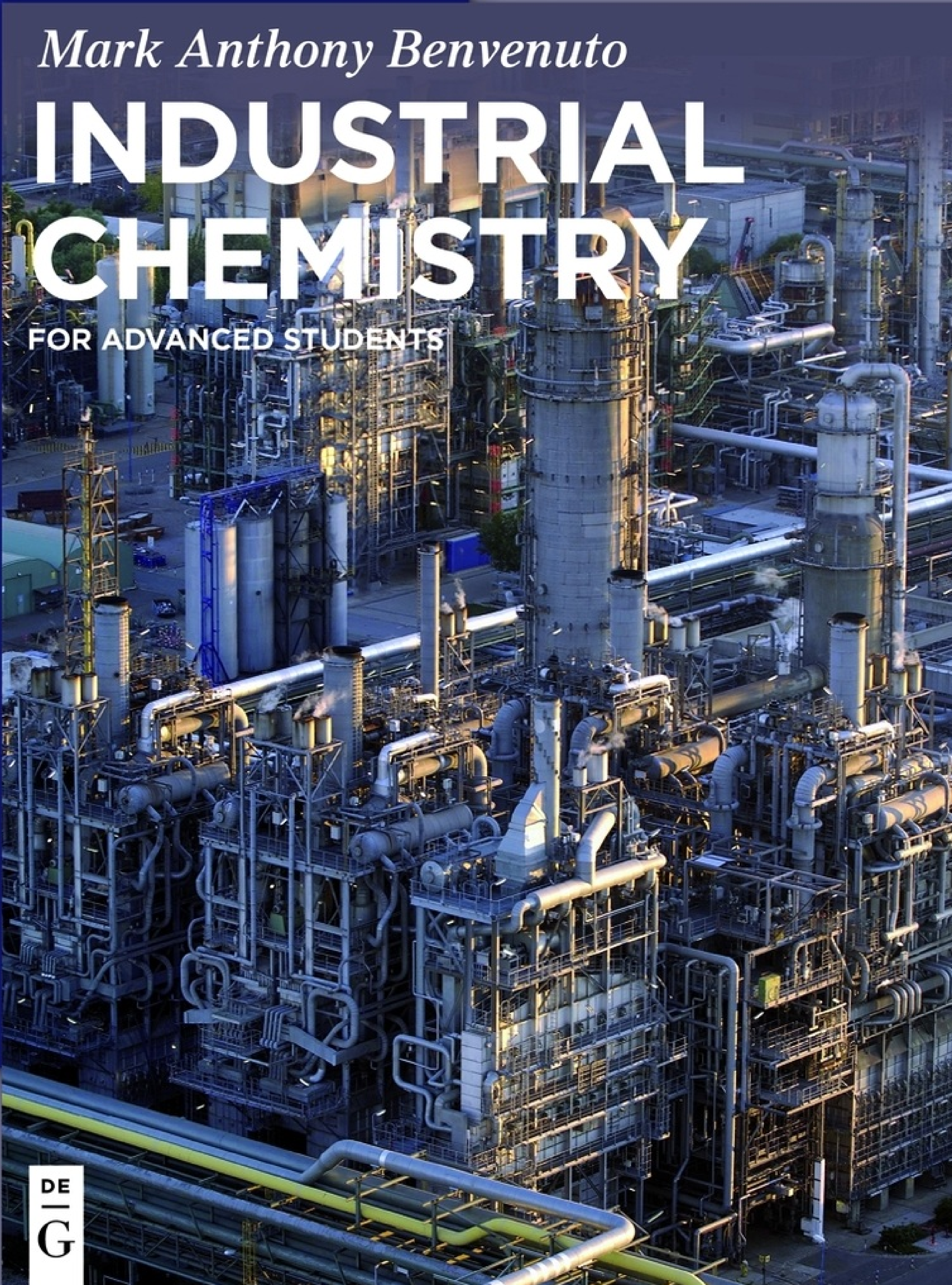

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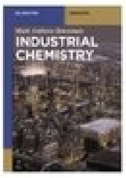

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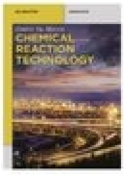

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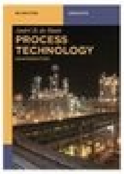

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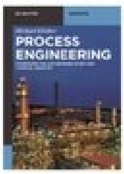

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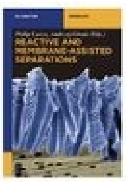

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For Advanced Students

DE GRUYTER

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Preface

The production of tens of thousands of commodity chemicals today yields a quality of life for many people which has never before been experienced throughout the rise and fall of all civilizations. Because of the ability to refine and use numerous chemicals from crude oil, we have a wide variety of long-lasting, durable plastics that help enable everything from modern medicine to long-distance food transport. This same source provides us with huge quantities of several different motor fuels which enable transportation that is far faster than anything that had been possible throughout most of history. Because of our ability to refine, isolate, and alloy more than 60 elemental metals, we have been able to do everything from creating new building materials to mass produce tiny magnets that enable cellular phones and a myriad of other electronic devices. Because of our ability to refine and use chemical commodities such as cement, concrete, and asphalt, we have been able to construct an infrastructure for humanity that again has never been accomplished, even in the most advanced cultures of the past.

Many of the largest produced commodity chemicals worldwide have been discussed in detail in the volume *Industrial Chemistry*. We will see in this book that many of the substances discussed in the first volume are used in chemical transformations that either produce or utilize the chemicals discussed here. But in writing a single volume, one has to make several painful choices about what is included, and what must be excluded, from the contents. *Industrial Chemistry – for Advanced Students* is not only picking up where *Industrial Chemistry* left off however; it is also widening the discussion and examination of the industrial-scale chemical processes and end products that make vital contributions to our world today. This volume's goal is to help students see the interconnectivity of a widely differing series of chemical processes and to relate what they have learned in other chemistry classes to the world of industrial-scale chemistry.

Writing a book like this is both a challenge and a reward, and there is probably no author alive who can do it without help. I have to thank my editors, Karin Sora and Julia Lauterbach for help and advice at every step of this book's development. Many of my work colleagues have been very helpful when it came to everything from chasing down the details of some process to double checking how ideas are presented in the chapters. Thanks are definitely due to Drs. Klaus Friedrich, Matt Mio, Liz Roberts-Kirchhoff, Shula Schlick, Mary Lou Caspers, Kate Lanigan, Kendra Evans, and Jon Stevens, and also to Jane Schley and Meghann Murray. Additionally, I thank Heinz Plaumann, Hulya Ahmed, and Denise Grimsley of BASF, Keith Olsen and Kevin Perry of General Motors, and Felix Schneider, formerly of the US Food and Drug Administration, for tolerating what may have seemed like an endless stream of apparently random questions from me. A very special thanks goes to Megan Klein of Ash Stevens for proof reading the entire manuscript. And obviously, many thanks go to my wife, Marye, and my sons, David and Christian, for just plain putting up with me as I wrote this book.

Detroit, January 2015

Mark A. Benvenuto

Table of Contents

1 Overview and introduction to the chemical industry

1.1 Focus and depth

Over 70,000 chemicals are produced annually on a large scale and are either used in some further chemical transformation, or are incorporated into an end product. Perhaps obviously, nothing short of an exhaustive encyclopedia could discuss all of them, or even list all their uses. Some focus is required in order to cover a selected series of topics within this extensive, broad field.

Similarly, it would be difficult to produce a volume that simply lists a series of chapters corresponding to the largest commodity chemicals used in the world today which were left out of *Industrial Chemistry*, because such a “laundry list” does little to place any of these chemicals and materials in a larger context. This book will attempt to discuss the large process chemistry omitted in the initial volume and will also build greater context among the processes. Thus, while there are chapters on chemicals that are certainly organic – those that are only produced from the refining of crude oil – as well as on those that are distinctly inorganic, there are also several chapters that straddle borders, such as hydrogen peroxide, food additives, bromine, fluorine, and asphalt.

Most developed nations track self-determined lists of materials that are deemed vital to their economies and defense. For example, in the United States, the Department of Energy maintains a *Critical Materials Strategy* (Department of Energy , 2014), the Department of Defense has published a *Strategic and Critical Materials 2013 Report on Stockpile Requirements* (Department of Defense, 2014), and the United States Geological Survey produces a *Mineral Commodities Summary* each year (United States Geological Survey, 2014). These reports indicate the quantities of various chemicals that are produced annually and how much the United States imports from other nations. Similar documents are produced by the ministries of defense, education, and economic growth in most European and Pacific nations. In addition to these, several national and internationally learned societies keep track of chemical and material production, and usually publish their own lists and compilations of statistics regarding them (Chemical and Engineering News, 2014; Royal Society of Chemistry, 2014; European Chemical Industry

Council, 2014; Society of Chemical Manufacturers and Affiliates, 2014; Gesellschaft Deutscher Chemiker, 2014; Chemical Society of Japan, 2014; Royal Australian Chemical Institute, 2014; International Union of Pure and Applied Chemistry, 2014). Also, trans-national organizations like the United Nations and the Arctic Economic Council monitor chemical production and industrial use in their annual reports and in more targeted documents (United Nations Environment Programme, 2012; United Nations Environmental Programme, 2014; Arctic Council, 2014).

The chemicals and materials in these chapters are not always produced on a large enough scale that they make it on to any "top 100" list of the above-mentioned organizations. But each material is vitally important in some way, and thus is worthy of discussion. Therefore, we have tried to include many of them in this book.

1.2 Recycling

There is no doubt that the chemical industry today has been greatly transformed from the industry of the 1960s. It has been noted that from 1945 to perhaps 1965, the generation that had fought the single largest war humanity had ever seen returned home and built a society and a quality of life that had also never been seen before. The infrastructure in the countries that had been embroiled in that war expanded greatly, which meant the use of millions of tons of refined metals, concrete, asphalt, glass, and petroleum products – the latter was in part for the fuels for the vehicles that made this all happen. Highways were constructed, cities built or rebuilt and water and energy infrastructures were put in place or replaced. All of this required massive amounts of chemicals and all of it generated waste.

The developed world has changed since that time. Now there is recognition that this level of man-made change has affected the world itself. While debate continues over resource depletion, climate change, the first priority use of arable land and the pollution of fresh and salt waters, the chemical industry has adapted and has moved toward cleaner, more environmentally benign practices for many of the production streams that manufacture and refine the chemicals we use today.

A part of each chapter in this book has been devoted to the concept of recycling and reuse of the material upon which it focuses. When no recycling or reuse is possible, this is acknowledged. But when some process has been improved, made safer, or made economically more sound through the practices of good stewardship on the part of producers, including recycling or reuse, that too is also acknowledged.

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2 Phosgene (carbonyl dichloride)

Throughout history, certain chemicals or materials have gained fame or notoriety for a wide variety of reasons. Gold has been valued in almost all civilizations from ancient times to the present for no reason except its visual beauty. Iron has been valued because of its ability to hold an edge, which makes it useful in forming tools and weapons. Arsenic and arsenic compounds have been known to be poisons in several cultures – and indeed, have been considered a weapon within an assassin's arsenal for hundreds of years. More recently, both phosgene and one of its starting materials, chlorine, have been considered one of the worst of battlefield weapons, namely, poison gas.

Elemental chlorine gas was indeed the first chemical warfare agent widely used on the western front of the First World War. Although the gas is poisonous, at the concentrations that were delivered by artillery in that war, it was seldom lethal by itself. It is denser than air, thus seeping and pouring into the trenches, forcing soldiers without gas helmets to rise up for air, where enemy soldiers could then shoot at them. Phosgene, used later in the war, was far more lethal. When inhaled even in small amounts, HCl forms in the lungs, affecting what is called "dry land drowning" as lung tissue was destroyed. The limited number of survivors of phosgene attacks claim that small doses of it smell like newly mown hay, or fresh-cut wheat.

It is staggeringly ironic than that elemental chlorine is today used as an inexpensive antibacterial in water, and thus has saved countless people from a wide variety of diseases. Even more so that phosgene is used as a starting material for several very useful plastics, all of which are produced in large volumes.

2.1 Method of production

The reaction chemistry that illustrates the synthesis of phosgene is a deceptively simple addition reaction. It can be represented as

$$Cl_{2(g)} + CO_{(g)} \longrightarrow COCl_{2(g)}$$

This does not however give any details about the reaction conditions, which are important for optimal yield of phosgene. The two reactants are passed through activated carbon, sometimes called activated charcoal. This serves a catalytic role. Since the reaction is exothermic and usually runs at a temperature zone of 50–150 °C, the reactor is typically cooled during the process.

The chlorine reactant is produced as one of the three products in what is called the chlor-alkali process. The other products of this process are sodium hydroxide and hydrogen gas. Carbon monoxide is usually produced by the reaction of carbon dioxide and carbon at elevated temperatures.

2.2 Volume of production annually

It is difficult to put a number on phosgene production annually, because the chemical's toxicity dictates that it is immediately used for the production of other commodity chemicals at the location at which it is generated. Because of its ability to be used as a chemical weapon, large producers must be reported to the Organization for the Prohibition of Chemical Weapons (Organization for the Prohibition of Chemical Weapons, 2014).

It is however possible to find the production figures for the more common isocyanates, which are produced from phosgene. Totaled, several million tons of the most common are produced annually.

2.3 Sales

Almost no phosgene is sold as a commodity chemical. Rather, most is produced at the site where it will be further used in the production of other commodity chemicals, such as diamines and isocyanates.

2.4 Uses

As mentioned, phosgene had an infamous debut, but has evolved into a highly useful starting material for several bulk, organic chemicals.

Today, the major use of phosgene is in the production of isocyanates, almost all of which are further used in the production of polyurethanes. While there are many isocyanates, methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI) are the two most commercially important, and thus the two that are made in the largest volumes. There are several large producers of MDI, including (in alphabetical order):

1. BASF, Germany
2. Bayer, USA
3. BorsodChem
4. Dow, USA
5. Huntsman
6. Nippon Polyurethane, Japan
7. OCI, South Korea
8. Yantai Wanhua, China, producing approximately 1.1 million tons (BASF Polyurethanes, 2014; Bayer Polyurethanes, 2014; BorsodChem, 2014; Dow, 2014; Huntsman Polyurethanes, 2014; Nippon Polyurethane Industry, 2013; OCI, 2013; Yantai Wanhua, 2013).

There are other, smaller producers as well (International Isocyanate Institute, 2013). For the past several years, roughly 5 million tons of isocyanates have been produced annually. The production of isocyanates is a matter of reacting an amine with phosgene. Generically, the reaction is as shown in Figure 2.1.

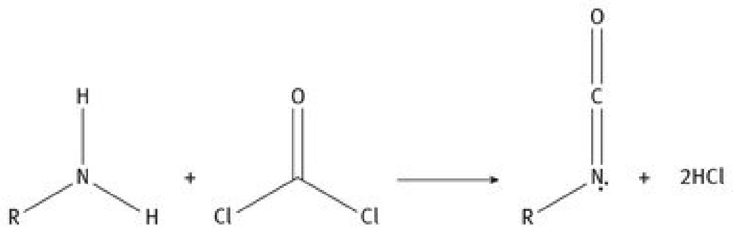

Fig. 2.1: Isocyanate production.

The more specific reaction to form MDI proceeds is shown in Figures 2.2 and 2.3.

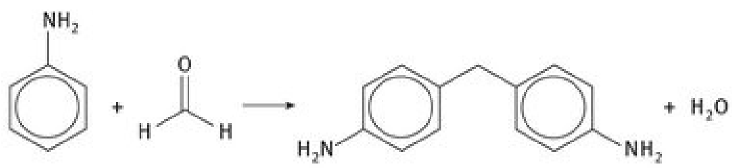

Fig. 2.2: Formation of methylene dianiline.

Aniline and formaldehyde form a precursor diamine. This is then reacted with 2 molar equivalents of phosgene to form the functional and reactive isocyanate ends, as seen in Figure 2.3.

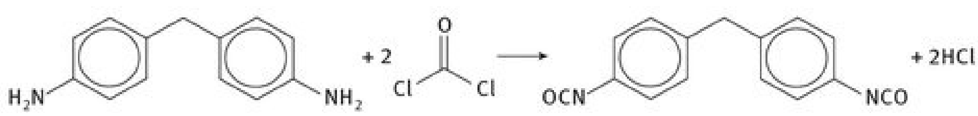

Fig. 2.3: MDI production.