

A NATIONAL HISTORIC
CHEMICAL LANDMARK

THE DISCOVERY OF ORGANIC FREE RADICALS BY MOSES GOMBERG

UNIVERSITY OF MICHIGAN
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AMERICAN CHEMICAL SOCIETY
Division of the History of Chemistry and
The Office of Communications



The Chemical Laboratory, University of Michigan, as it looked in 1877. Moses Gomberg did his early work on organic free radicals here. The laboratory opened in 1856, the first at a state university to be used solely for chemistry. It was destroyed by fire in 1981.

This booklet commemorates Moses Gomberg's discovery of organic free radicals as a National Historic Chemical Landmark. The designation was conferred by the American Chemical Society, a nonprofit scientific and educational organization of 161,000 chemists and chemical engineers. ACS presented a plaque marking the event to the University of Michigan on June 25, 2000, during a celebration of the 100th anniversary of Gomberg's seminal discoveries. The inscription reads:

“In 1900, Moses Gomberg, Professor of Chemistry at the University of Michigan, confirmed the existence of a stable, trivalent organic free radical: triphenylmethyl. In so doing, he challenged the then prevailing belief that carbon could have only four chemical bonds. Gomberg's discovery made a major contribution to theoretical organic chemistry and fostered a field of research that continues to grow and expand. Today, organic free radicals are widely used in plastics and rubber manufacture, as well as medicine, agriculture and biochemistry.”

On the cover: Moses Gomberg in 1890 while a graduate student at the University of Michigan.

Acknowledgments:

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ORGANIC FREE RADICALS

Moses Gomberg, a chemistry professor at the University of Michigan, discovered an organic free radical in 1900 and affirmed what had been thought impossible. A century later, free radical organic chemistry researchers look back to Gomberg as the founder of their field. His work led to modern theories of the structure and reactivity of organic molecules — theories whose application has had tremendous impact on modern life.

We now know that organic free radicals are essential to the way in which some enzymes function in the human body. We know that organic free radicals are involved in the body's aging process, in its healthy functioning, and in the development of cancer and other serious diseases. Understanding organic free radicals has helped us explain DNA synthesis in the body and many other natural phenomena, from food spoilage to the effects of sunburn. Organic free radicals also play a major role in the production of plastics, synthetic rubber, and other widely used synthetic materials.

What is an Organic Free Radical?

Atoms form molecules by sharing electrons, and electrons pair up with one another. Each pair of electrons constitutes a chemical bond. Most molecules contain an even number of electrons.

A *free radical* is an atom or a group of atoms with an odd number of electrons. The odd, unpaired electron in a free radical seeks to pair (form a bond) with another electron. A free radical readily reacts with another atom or group of atoms. Most free radicals are so reactive they exist only for a fleeting moment.

Organic molecules contain carbon, which very readily forms four electron pairs (bonds) when reacting with other atoms or molecules. An *organic free radical* is a free radical form of carbon with three bonds and a single, unpaired electron.

A free radical can react with another free radical, but more often it reacts with a stable, evenly paired molecule. It does so by (1) donating an electron to the molecule, (2) removing an electron from the molecule, (3) removing a group of atoms from the molecule, or (4) adding itself to the molecule. When a free radical reacts with a stable molecule in these ways, it turns the stable molecule into a free radical. This can set in motion a chain reaction of free radical formation.

Gomberg's Breakthrough

Nineteenth century scientists speculated that there could be a free radical containing carbon — an *organic free radical*. But after many attempts to isolate it failed, they concluded they were wrong and that carbon must always be tetravalent (form four bonds).

Moses Gomberg was trying to synthesize a carbon compound called hexaphenylethane when he inadvertently synthesized triphenylmethyl (trityl for short), a mysterious, highly reactive, unstable substance (see illustration on page 2). He recognized that he had found the long-elusive free radical and showed that carbon is not always tetravalent — the then prevailing view.

Gomberg published his findings in 1900, but the existence of triphenylmethyl and other organic free radicals remained in dispute for nearly a decade. They were viewed as a curiosity even after the scientific community recognized their existence. Not until the 1930s did free radicals enter the mainstream of organic chemistry.



Moses Gomberg

THE DISCOVERY OF TRIPHENYLMETHYL

Moses Gomberg studied analytical chemistry at the University of Michigan and synthetic chemistry in Germany, then the world's main center of chemical research. That combination of experience equipped him to recognize his historic discovery for what it was.

At Adolf Baeyer's laboratory at the University of Munich, Gomberg worked closely with Johannes Thiele, whose partial valence theory explained organic compound reactivity by assigning partial bonds to carbons in chains with alternating single and double bonds. Earlier, Baeyer had succeeded in synthesizing organic compounds with August Kekulé, but not tetraphenylmethane. Several prominent chemists, among them Victor Meyer, had also failed in their attempts to synthesize tetraphenylmethane. They concluded it was inherently unstable.

At the University of Heidelberg, where he worked with Meyer, Gomberg took a different approach based on Thiele's work. He succeeded where others had failed and obtained a tiny

amount of tetraphenylmethane.

Gomberg returned to Michigan, where he improved the yield slightly. He then tried to produce the next fully phenylated hydrocarbon — hexaphenylethane — by reacting triphenylmethyl halides with sodium in benzene. When this failed, he repeated the experiment using silver instead of sodium. He obtained a white crystalline powder that reacted with oxygen in the air.

To avoid this oxidation, Gomberg reacted triphenylmethyl chloride and zinc in an atmosphere of carbon dioxide. Sometimes, he allowed the experiment to run for weeks in a special airtight apparatus he had constructed. The reaction produced a thick, dark yellow syrup.

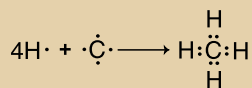
Gomberg removed the benzene solvent at reduced pressure, leaving behind a white solid of unexpectedly high reactivity. It oxidized rapidly in the air and reacted readily with halogens, including iodine. These properties were not what Gomberg expected from hexaphenylethane. "The experimental evidence ... forces me to the conclusion that we

CARBON BONDS

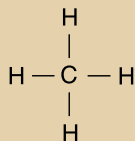
Carbon atoms have four electrons capable of forming chemical bonds. As shown below, they are usually depicted as dots.



A covalent chemical bond is formed when atoms share a pair of electrons. For example, hydrogen has one electron and carbon has four electrons in the grouping known as methane, the main constituent of natural gas. As shown below, four covalent bonds can be formed between the carbon and hydrogen atoms.

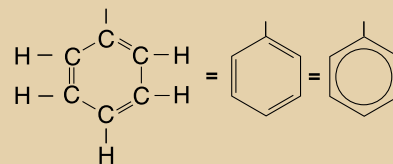


When carbon has four bonds, it is called **tetravalent**. A simpler, compressed representation is CH_4 . As shown at right, dashes rather than dots can be used to represent pairs of electrons.

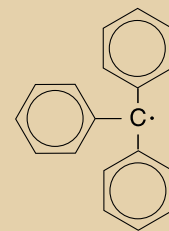


When carbon has three bonds instead of four, it is called **trivalent**. This grouping is known as the methyl radical. As shown at left, if a carbon atom had just three bonds to hydrogen atoms, one electron would remain unshared and unpaired.

The phenyl group is very important to organic chemistry. As shown below, it consists of six carbon atoms bonded to five hydrogen atoms, with double bonds (four electrons) between some of the carbon atoms.



Moses Gomberg discovered triphenylmethyl, the first organic free radical with a measurable lifetime. As shown at right, three phenyl groups replace the three hydrogen atoms of the methyl group in triphenylmethyl.



Triphenylmethyl
(note the unpaired electron represented by the dot)



Moses Gomberg, (center), with students, 1915. Chester S. Schoepfle, (second from the right), succeeded Gomberg as chairman of the chemistry department in 1936.

have to deal here with a free radical, triphenylmethyl,” he wrote in his published findings. “On this assumption alone do the results described above become intelligible and receive an adequate explanation. ... The radical so formed is apparently stable, for it can be kept both in solution and in the dry crystalline state for weeks.”

Gomberg published his findings in 1900 in the *Journal of the American Chemical Society* and in Germany’s *Berichte der Deutschen Chemischen Gesellschaft*. Publishing simultaneously in English and German was a common practice at the time among U.S. scientists with links to Germany. It was also common to designate oneself the proprietor of a new field, as Gomberg did in the conclusion of his paper: “This work will be continued and I wish to reserve the field for myself.”

Other chemists greeted Gomberg’s discovery with skepticism. Most remained convinced that carbon must be tetravalent — understandable given that the explanation, electronic bonding, would not be articulated until years later by scientists such as G.N. Lewis, Walter Kossel and Irving Langmuir.

A Wide-Reaching Legacy

The scientific community began recognizing the importance of free radicals in 1929, when Friedrich Paneth and Wilhelm Hofeditz produced the methyl free radical, CH_3 . Unlike the trityl radical, the methyl radical was elusive and could not be isolated. This showed that organic free radicals can exist momentarily and suggested that many chemical reactions involve free radicals.

In 1933, Morris Kharasch and his student, Frank Mayo, invoked a free-radical mechanism and discovered “the peroxide effect,” which they subsequently applied to other chemical systems. Their

work, coupled with that of Gomberg and others, paved the way to development of synthetic materials ranging from rubber to plastics.

Conventional polymerization continued to be used to produce nylon and other products. But free radical polymerization had advantages such as high tolerance of chemical impurities and extreme temperatures, and the ability to be used with a wide range of monomers (organic molecules). Today, free radicals are used to produce nearly half the polymers we use — materials used in everything from food wrapping to paint, adhesives, film, carpeting, piping, and more.

In medicine, understanding free radicals, particularly those formed by oxygen, has illuminated the nature of oxidative stress — damage that results when free radicals form faster than the body removes them. This, in turn, has revealed ways human health can be improved — for example, by using antioxidants. We now recognize that many free radicals are essential components of enzymes in the body, while others can damage DNA, leading to cancer or other diseases. We know, for example, that free radicals formed by excessive exposure to the sun’s ultraviolet light can lead to cataracts.

Many free radical processes involve chain reactions that begin when an unpaired electron fails to find another unpaired electron with which it can easily bond. The free radical removes an atom (usually hydrogen) from another molecule, turning itself into a stable molecule; the molecule it attacked becomes a free radical. Such chain reactions are used to make environmentally friendly products such as recyclable automobile tires and soaps free of salts.



Boys’ classical gymnasium located on Petrovskaya Street in Elizavetgrad, Russia, (now named T. C. Shevchenko Street, Kirovograd, Ukraine). Moses Gomberg was a student here from the first through the sixth grades.

MOSES GOMBERG (1866-1947)

Moses Gomberg was born on February 8, 1866 in Elizavetgrad, Russia, a town south of Kiev now known as Kirovograd, Ukraine. Because the family was Jewish, it received harsh treatment after the assassination of Tsar Alexander II in 1881. The government accused Gomberg's father of anti-tsarist activities and confiscated the family farm in 1884.



The 18-year-old Gomberg also fell under suspicion.

The family fled to the United States, settling in Chicago, Illinois. There, young Moses followed the classic immigrant path to success. Speaking no English, he worked at odd jobs, most involving menial labor. He toiled in the Chicago stockyards under the brutal conditions described in Upton Sinclair's novel, *The Jungle*.

Through sheer force of will and brainpower, Gomberg learned

English, completed his secondary education, and in 1886 entered the University of Michigan. He tried to enroll in a beginning course in physics, but the department head turned him down because he had no formal training in trigonometry. Three days later, he tried again. When the department again rejected him for the same reason, Gomberg insisted he knew the subject. The department head quizzed him, and was stunned to find that what he claimed was true.

Gomberg earned his Ph.D. in 1894 and remained at Michigan for the rest of his professional life, except for a year spent in Germany and a summer at the University of California. Widely regarded as a fine teacher and lecturer, he was appointed an assistant professor in 1899 and a full professor in 1904; he chaired Michigan's chemistry department from 1927 until he retired in 1936.

Gomberg lived quietly, sharing a house in Ann Arbor with his sister, Sonia. Her health began to fail around the time of his retirement, and he spent most of the rest of his life caring for her. He died on February 12, 1947, four days after his 81st birthday.

Those who knew Gomberg remembered him as kind, generous and modest, as well as a man with strong convictions. He was unfailingly courteous. Students often tried — in vain — to follow him through a door.

Gomberg was known for his dry wit. A policeman in Ann Arbor stopped him for rolling through a stop sign and sternly said, "The next time, I want you to come to a complete stop!" Gomberg politely replied, "Is there any other kind of stop?"

Although Gomberg is best known for his discovery of organic free radicals, he made many other contributions to organic and applied chemistry. He developed new solvents for automobile lacquers, the first antifreeze compound used in cars, and a procedure for producing mustard gas during World War I.

He received honorary degrees from the University of Chicago, Brooklyn Polytechnic Institute, and the University of Michigan, as well as three medals from the American Chemical Society: the Nichols Medal in 1914, the Willard Gibbs Medal in 1925, and the Chandler Medal in 1927. He was elected to the National Academy of Sciences in 1914, and served as president of the American Chemical Society in 1931.

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THE NATIONAL HISTORIC CHEMICAL LANDMARKS PROGRAM

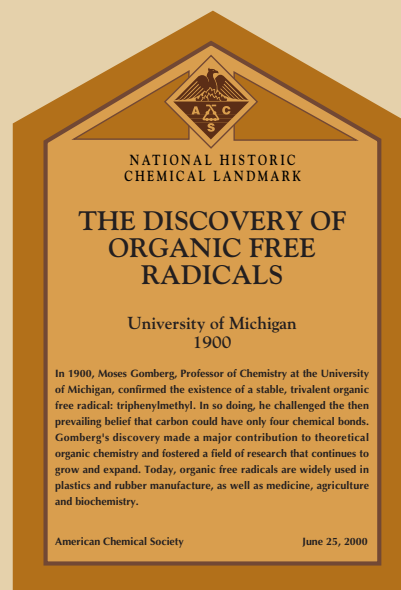
The National Historic Chemical Landmarks Program recognizes our scientific and technical heritage and encourages the preservation of historically important achievements and artifacts in chemistry, chemical engineering, and the chemical process industries. The program provides an annotated roster to remind chemists, chemical engineers, students, educators, historians, and travelers of an inspiring heritage that illuminates both where we have been and where we might go when traveling the diverse paths to discovery.

A historic chemical landmark represents a distinctive step in the evolution of chemical science and technology. Designations of sites and artifacts note events or developments of clear historical importance to chemists and chemical engineers. Collections mark the contributions of a number of objects with special significance to the historical development of chemistry and chemical engineering.

The Division of the History of Chemistry began this program in 1992. An international ACS committee, composed of chemists, chemical engineers, and historians of science and technology, works with the Office of Communications and is assisted by the Chemical Heritage Foundation. Together, these organizations provide a public service by examining, noting, recording,

and acknowledging particularly significant achievements in chemistry and chemical engineering.

For further information, please contact the ACS Office of Communications, 1155 Sixteenth Street, N.W., Washington, D.C. 20036; 800-227-5558, ext. 6274; e-mail: nhclp@acs.org.



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