

## CUPRENE: A HISTORICAL CURIOSITY ALONG THE PATH TO POLYACETYLENE

Seth C. Rasmussen, Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND, seth.rasmussen@ndsu.edu

### Introduction

The historical importance of polyacetylene was cemented in 1977, when a collaboration between Hideki Shirakawa, Alan G. MacDiarmid, and Alan J. Heeger at the University of Pennsylvania revealed that it was possible to achieve metallic conductivity from free-standing films of the conjugated organic polymer when treated with oxidizing agents such as  $I_2$  or  $AsF_5$  (1-8). Although previous studies on oxidized conjugated polymers such as polypyrrole, polyaniline, and polyacetylene (Figure 1) had revealed conductivities in the semiconducting range (6-9), the ability to generate metallic conductivities from an organic plastic seemed to promise a wealth of possible new applications and brought unprecedented attention to these conducting organic polymers. In recognition of this, the 2000 Nobel Prize in Chemistry was awarded to Shirakawa, MacDiarmid, and Heeger for their pioneering work with polyacetylene and their early contributions to the field of conjugated organic polymers (10).

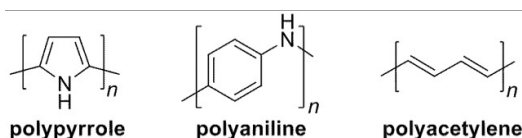


Figure 1. Conducting conjugated polymers under study between 1963 and 1979.

Although the most structurally simple of the conjugated polymers, polyacetylene is not nearly as old as other conjugated materials such as polyaniline or polypyrrole (6-9). In fact, it was not until 1955 that Giulio Natta (1903-1979) reported the first successful production of polyacetylene (11, 12). As outlined in Figure 2, Natta's methods utilized combinations of triethylaluminum ( $Et_3Al$ ) and titanium(IV) propoxide ( $Ti(OC_3H_7)_4$ ) to catalytically polymerize the gaseous acetylene to a black crystalline polymeric product (12).

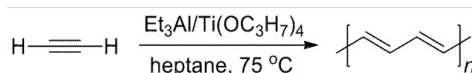


Figure 2. Natta's catalytic polymerization of acetylene.

Although not prepared directly from acetylene, oligomeric analogues known as polyenes ( $-CH=CH-$ )<sub>n</sub> predate Natta's work, with the phenyl-capped series **1a-d** (Figure 3) prepared as early as 1928 (13-16). Such polyenes were typically limited to shorter oligomers ( $n = 2-10$ ) and were used to correlate physical and optical properties with conjugation length (13-17).

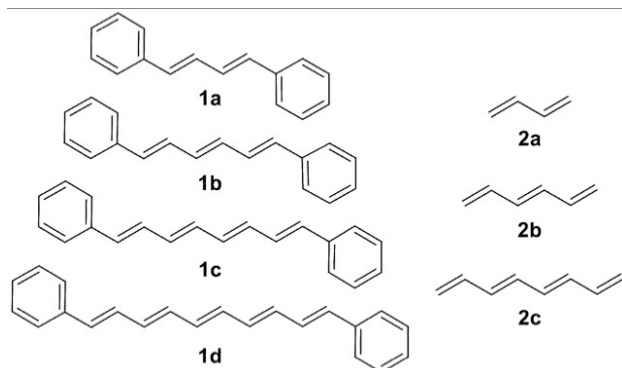


Figure 3. Early polyene series.

This is not to say that polymerization attempts did not predate Natta's success in 1955. Prior to all of these efforts, various researchers had investigated the polymerization of acetylene with the earliest reports appearing in the late 1860s (18, 19). These efforts resulted in the production of a resinous material that was ultimately named *cuprene*. The composition and structure of this material was the subject of much debate, however, and to date its history has been poorly detailed (12, 20-22). As such, the current report aims to present the first detailed history of these early polymerization attempts from 1866 through the late 1930s when interest in this material began to decline. This discussion will thus begin with the work of Marcellin Berthelot (1827-1907) in 1866 (18, 19).

### Berthelot, Acetylene, and Initial Polymerization

Pierre Eugène Marcellin Berthelot (Figure 4) was born in Paris on October 25, 1827 (23, 24). The son of a medical doctor, he received the *Baccalauréat ès Lettres* required for entrance to the university in 1846. Two years later, he was awarded the *Baccalauréat ès Sciences* and as holder of two Baccalauréats, he was entitled to undertake studies in both the arts and science. He pursued his studies at the Collège de France (23, 24), where he ultimately focused on science and earned the degree of *Licence ès Physique* on July 26, 1849 (23). Berthelot then entered a private school for the practical teaching of chemistry founded by Théophile Jules Pelouze (1807-1867), former assistant to Joseph Louis Gay-Lussac (1778-1850). At the school, Berthelot supervised the student's work, but was otherwise free to experiment and he published his first two articles in 1850 (23).

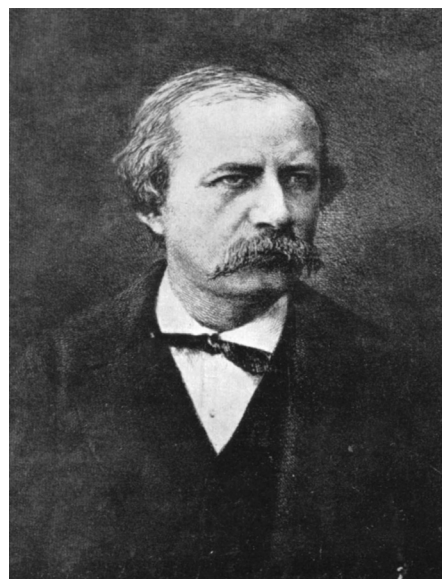


Figure 4. Pierre Eugène Marcellin Berthelot (1827-1907) [Edgar Fahs Smith Collection, University of Pennsylvania Libraries]

Berthelot then returned to the Collège de France in February 1851, where he joined Antoine Balard (1802-1876) as his assistant in charge of lecture demonstrations. Finally, he submitted his thesis for the *Doctorat ès Sciences* in April of 1854, after which he registered at the Ecole Supérieure de Pharmacie. He submitted a second thesis for the *Doctorat en Pharmacie* in November of 1858, while also acquiring the diploma of *Pharmacien de Première Classe* (23). Due to the intervention of Jean-Baptiste Dumas (1800-1884), a chair of organic chemistry was created at the Ecole Supérieure de Pharmacie in December of 1859. Coincidentally, Berthelot had just acquired the prerequisites for the position and he thus became the first Titular Professor of the chair and held the position until 1876 (22, 24).

It was in 1860 (25), shortly after assuming the chair of organic chemistry, that Berthelot reported studies on a new carbon-hydrogen gas (26) which he gave the name *acétylène* (25, 27). He was able to produce the gas by passing various organic gases or vapors (ethylene, alcohol, ether, etc.) through a red-hot tube and into an ammonia solution of cuprous chloride (Figure 5). This resulted in the precipitation of a red copper acetylide, which could be collected and then treated with HCl to liberate the acetylene gas (24, 25, 27). In addition to careful characterization of the acetylene gas, Berthelot thoroughly investigated its reactivity via the production of a series of chemical derivatives (25, 27).

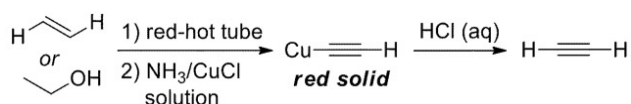


Figure 5. Berthelot's initial synthesis of acetylene.

Continuing with these efforts, he then reported in 1862 the production of acetylene via an electric discharge between two carbon rods in the presence of hydrogen (23, 27, 28). As before, the acetylene product was trapped in an ammonia solution of cuprous chloride and the isolated copper acetylide was then treated with HCl to liberate the pure acetylene gas. This now allowed Berthelot to generate large amounts of acetylene, with a reported production rate of 10 mL per min (27, 28).

The following year, Berthelot was entrusted with the lectures on organic chemistry at the Collège de France in addition to his teaching at the Ecole Supérieure de Pharmacie (23). In August of 1864, he then advanced to occupy a new chair of organic chemistry created for him at the Collège. He retained this chair until his death in 1907 (23, 24).

In 1866, Berthelot started a series of studies on the action of heat upon acetylene (18, 19, 24). Upon heating acetylene at extreme temperatures (described as the temperature at which glass softens or melts), Berthelot observed the formation of a mixture of two products which he described as follows (18):

These consist primarily of two carbides: one volatile and which has the properties and reactions of styrene ... the other almost fixed, resinous, and which appears to be metastyrol.

The term *metastyrol* refers to the product formed by the polymerization of styrene and was thus an early term for polystyrene (29, 30). As such, one could infer that the resinous product here is polymeric material of some form. Analysis of the volatile product, a yellowish liquid, revealed that it consisted primarily of benzene (19).

Berthelot continued this work by heating acetylene in the presence of various species, including elemental carbon or iron. It was found that the presence of these species significantly decreased the temperature required to cause reaction, while simultaneously increasing the overall reaction rate and influencing the nature of the products generated. He ultimately concluded (18):

In summary, the transformation of acetylene by heat is not comparable to the phenomena of dissociation: it is not the result of a destruction of the affinity that holds together carbon and hydrogen; but it shall be by a very different mechanism, which is not incom-

patible with the stability of acetylene. What the heat determines here, it's not a decomposition, it is rather a combination of a higher order, developed by the mutual union of several acetylene molecules.

Further studies of acetylene polymerization reactions, however, were not reported until the 1874 work of Paul Thenard (1819-1884) and Arnoult Thenard (1843-1905) on the effect of electric discharge on acetylene gas (31).

### The Thenards and the Action of Electric Discharge on Acetylene

Arnoult Paul Edmond Thenard (32) was born either October 6 (33), December 6 (34), or December 16 (35), 1819 in Paris, the oldest son of the well-known French chemist Louis Jacques Thenard (1777-1857) (33-38). A baron and wealthy landowner (34, 35), Paul was an eminent chemist who submitted his first paper to the Academy of Sciences in 1844 (33-35). Paul married a Miss Derrion-Duplan on October 24, 1842. On January 16, 1847, the uncle of his new wife passed away, leaving her the sole heir to the chateau and land of Talmay, Côte-d'Or. The young couple thus moved to Talmay, where Paul installed a laboratory in the vast commons of the chateau (34). Here, he carried out much of the agricultural chemistry research for which he was known (33-37). The extent of this work resulted in his election to the Paris Academy of Sciences in 1864, where he became one of its most active members (33-36). He was also a member of the French National Society of Agriculture (34).

During the Franco-Prussian War, Paul was taken from his home as a hostage, and transported to Bremen along with several other notables of Côte-d'Or (34-36). His wife followed him (34, 35) and they remained there until the conclusion of peace (35). Paul also served as general counsel for the Côte-d'Or commune of Pontailler until 1871 and was made a Knight of the National Order of the Legion of Honour (35). Paul died as a result of apoplexy at his Talmay chateau on August 8, 1884 (33, 36).

Less is known of the younger Arnoult Thenard. He was born in Givry, Saône-et-Loire, to Paul and his wife during the first year of their marriage in 1843 (34). His father initiated him to laboratory life at an early age and he went on to pursue the study of medicine in the service of the French physician and surgeon Auguste Nélaton (1807-1873) (34). After his time with Nélaton, he returned to his father's laboratory to collaborate on various projects. The Franco-Prussian War interrupted his scientific pursuits and he joined the French army to serve

as a doctor and liaison through enemy lines (34, 35). After the Battle of Sedan, he moved to Belgium and joined the Armée de la Loire (34). Eventually, he returned to his experimental work, which spanned chemistry, agriculture, and medicine. He was ultimately elected a member of the French National Society of Agriculture (35).

Beginning in 1873, the Thenards began studying the influence of electric discharge on various gaseous mixtures (39, 40). Their initial efforts were supported by the assistance of Edmond Fremy (1814-1894) and Berthelot in order to study discharge tubes containing mixtures of either marsh gas and carbonic acid or carbon monoxide and hydrogen (39). This first report was then followed by a second 1873 paper (40) which expanded the number of gases studied before turning to acetylene in a publication in late January of 1874 (31).

Using a discharge device designed by Arnould, they found that the electric discharge caused a rapid condensation of acetylene ( $4\text{-}5\text{ cm}^3\text{ min}^{-1}$ ) resulting in a solid deposit on the walls of the unit (31). They described the solid as very hard, with a glassy appearance and a color they compared to the dregs of wine. Analysis of the solid gave a formula consistent with that of acetylene gas (i.e.,  $(\text{C}_2\text{H}_2)_n$ ). No solvent was found that was able to dissolve the material, nor did nitric acid have any effect on the solid. Attempts to separate or purify the material by distillation also failed, resulting in the conclusion that the solid was analogous to bitumen. This view was shared by Berthelot (31).

The work by the Thenards was then quickly followed up with two closely related studies. The first of these studies was by the Belgian P. De Wilde later that same year (41), while the second was three years later by Berthelot himself in 1877 (42).

### Additional Discharge Studies of De Wilde and Berthelot

Not much is known about De Wilde (Figure 6), with even his given name being unknown beyond the initial "P" (43). What is known is that he was professor of chemistry at the Agricultural Institute of the State in Gembloux, Belgium (44-47), where he taught general chemistry, analytical chemistry, physics, agricultural technology, and meteorology (46, 47). The Institute had been established in 1860 with G. Michelet as the first professor of chemistry and physics (47). De Wilde replaced Michelet sometime before 1865 (44, 45) and was ultimately replaced by L. Chevron in 1867 (46).



P. DE WILDE

Figure 6. P. De Wilde (46).

Beginning in 1865, De Wilde started reporting research on acetylene, with initial efforts focusing on the preparation of acetylene from ethylene chloride or 1,2-dichloroethane (44, 45). He then continued with research into the reactions of acetylene and hydrogen in the presence of platinum black. Although this early work was reported in the Dutch literature, he then published a paper in *Berichte der Deutschen Chemischen Gesellschaft* in which he first presented a summary of his earlier reports, followed by the presentation of new work on the effect of electrical current on various gases and gas mixtures (41). This paper was published in the spring of 1874 and De Wilde began his description of the electrical experiments with a statement that the previous work of the Thenards was the inspiration for his efforts in this area.

De Wilde first studied the effect of electrical current on mixtures of sulfur dioxide and oxygen before moving on to pure samples of ethylene or acetylene (41). In the case of acetylene, he expected to generate benzene and styrene products similar to that found by Berthelot upon heating acetylene at high temperatures, but states that his experiments did not confirm this. Instead, he reported that the current caused the condensation of an oily yellow liquid on the walls of the discharge tube, which solidified after a few hours to produce a hard, amorphous, yet brittle, brown material (41). As with the product of the Thenards, no solvent was found to dissolve the brown material, but De Wilde did find that it burned to leave behind a coal-like residue.

De Wilde's comment that his efforts did not give the expected products of Berthelot is odd and one can only assume that he was not aware that Berthelot produced a resinous material in addition to the liquid polymerization

products. De Wilde stated that he intended to continue studying this interesting solid, but expected the necessary studies to be quite time consuming and thus wanted to report his initial findings (41). De Wilde, however, did not seem to follow up on this initial report.

Berthelot then followed these reports with his own study on the effect of electric discharge on acetylene, three years later in 1877 (42). Repeating the conditions of the Thenards, he verified the accuracy of their report and tried to provide some additional detail. Berthelot described the solid material as a brown polymer with the formula  $(C_4H_2)_n$ . Heating the material under  $N_2$  caused it to break down exothermically to give styrene, a carbonaceous residue, and other gaseous byproducts. He stated that this reactivity distinguishes it from all other known acetylene polymers (42), but did not directly compare these results to his previous reports of the thermal polymerization of acetylene.

After this flurry of acetylene polymerization studies between 1866 and 1877, no further reports appeared for the next 20 years. This changed in 1898, however, with the report of a new thermal polymerization study by Hugo Erdmann (1862-1910) and Paul Köthner (48).

### Erdmann and Polymerization over Copper

Hugo Wilhelm Traugott Erdmann was born in East Prussia on May 8, 1862 (49). Beginning in 1879, he studied chemistry at Halle, Munich and Straßburg under Wilhelm Heintz (1817-1880), Adolf von Baeyer (1835-1917), Emil Fischer (1852-1919), and Rudolf Fittig (1835-1910). He completed his doctorate at Straßburg in 1883 and then habilitated in 1885 under Jacob Volhard (1834-1910) at Halle. He became the director of the Laboratory of Applied Chemistry at Halle in 1899 and was then called to Berlin in 1901 as head of the Laboratory on Inorganic Chemistry of the Institute of Technology. He made significant contributions to both organic and inorganic chemistry, but is best known for coining the term "noble gases." He died in a boating accident on the lake Müritzssee at the relatively young age of 48 (49).

In late 1898, Erdmann and Paul Köthner reported a series of studies involving the heating of acetylene over copper metal (48). They found that although a temperature of  $780^\circ C$  is required to cause the thermal reaction of acetylene, this temperature could be significantly reduced when carried out in the presence of copper. When acetylene was passed over copper powder at  $400\text{--}500^\circ C$ , small crystals of graphite were found to form on the copper

surface. If the temperature was maintained below  $250^\circ C$ , however, graphite formation was not observed and the production of a light brown solid occurred instead (22, 48). It was found that this material could also be produced in a similar manner, although at a much faster rate, by using copper oxide in place of copper powder.

This light brown material was found to be very light and bulky, with a density of ca.  $0.023\text{ g/mL}$ . The material was treated in dilute boiling hydrochloric acid and filtered, after which the colorless filtrate was treated with sodium hydroxide to precipitate yellow copper hydroxide. As such, this led to the conclusion that this material was a copper compound of some form. Combustion analysis then led to the formula of  $C_{44}H_{64}Cu_3$  (22, 48). These collected analyses led to the conclusion (48):

There have been analyses of different preparations, which give such well-matched values that we should not hesitate to address these light brown copper acetylene compounds as a single, albeit very complex composite compound.

This study was then followed by a related conference report in May of the following year by Paul Sabatier (1854-1941) and Jean Senderens (1856-1937) (50).

### Sabatier and Cuprene

Paul Sabatier (Figure 7) was born at Carcassonne, France on November 5, 1854 (51-53). He received his primary education at a lyceum in Carcassonne, followed by a move to a lyceum in Toulouse in 1868 (52, 53). He graduated first in his class at the Ecole Normale Supérieure in 1877 (52,53), after which he taught for a year at the Lycée of Nîmes (52). He then became an assistant to Marcellin Berthelot at the Collège de France in 1878 and presented a thesis on the thermochemistry of sulfur and the metallic sulfides in 1880, for which he received the degree of Doctor of Science (51-53).

After a year spent in the Faculty of Sciences at Bordeaux, he took charge of a course in physics at the University of Toulouse in January 1882 (51, 52). A year later, he took charge of an additional course in chemistry before becoming Professor of Chemistry in November 1884 (52, 53). In 1908, Sabatier was invited to fill the position of Henri Moissan (1852-1907) at the Sorbonne, as well as Berthelot's position at the Collège de France, but he declined both to remain in Toulouse (53).

Sabatier was awarded the Lacaze prize of the Academy of Science of Paris in 1897 (51, 52) and was then elected a corresponding member of the Academy in 1901



**Figure 7.** Paul Sabatier (1854-1941) (right) with Edgar Fahs Smith [Edgar Fahs Smith Collection, University of Pennsylvania Libraries]

(52, 53). In 1905, he was awarded the Jecker prize by the Academy (51, 52) and also became Dean of the Faculty of Sciences at the Collège de France (51, 53). For his contributions to the hydrogenation of organic compounds via heterogeneous catalysis, he was awarded the 1912 Nobel Prize in chemistry, which he shared with Victor Grignard (1871-1935) (51-53). The following year, he was made a full member of the Paris Academy of Sciences (52, 53). He then received the Davy Medal from the Royal Society in 1915, to which he was elected as foreign member in 1918 (51, 52). Sabatier finally retired from his professorship in 1930 (52, 53). Although retired, Sabatier had special authorization to continue lecturing, which he did almost to the end (52, 53). He died at Toulouse on August 14, 1941, at the age of 86 years (51-53).

At the May 12, 1899, meeting of the Chemical Society of Paris, Sabatier presented initial results obtained with his collaborator Jean P. Senderens, in which they found that heating acetylene with copper at ca. 180°C produced a yellow-brown material (50). This material, which they described as a complex hydrocarbon, was very light and voluminous with small traces of dispersed copper. This was then followed up with a report published in *Comptes Rendus* the following year (54). Here, they describe the thermal reaction of acetylene with copper in significantly more detail. When a stream of acetylene was passed through a tube containing copper at low temperature, no reaction was observed. When the temperature was raised to 180°C, however, the copper turned brown and the pressure decreased due to condensation of

acetylene. As the process continued, the copper would gradually take on a darker hue and the mass swelled to fill the tube, completely closing off the passage of gas. It was found that if a small amount of brown substance was smeared into a fresh tube and heated to 180-250°C in a stream of acetylene, expansion would begin again, with the material swelling once again to fill the entire tube. This process could be repeated three to four times before no additional reaction was observed (54).

The material prepared in this manner was described as a dark yellow solid, which appears to be composed of a thin twisted filament assembly when viewed under a microscope (54). The material was described as soft and lightweight, yet a slight compression can give it the consistency and look of wood. No solvents were found that could dissolve the material, but the material burned to give off an aromatic odor and smoky flame, leaving a black residue of cupric oxide. It was concluded that the material was a hydrocarbon in which small amounts of copper (1.7-3%) were distributed. Multiple analyses led to an empirical formula of  $C_7H_6$ . Due to the origin of the material, they proposed to name it *cuprene* (54).

They admitted that they rushed the publication of the study due to a similar report by Hans Alexander (55), which they became aware of after Alexander's paper was highlighted in the *Bulletin de la Société Chimique de Paris* in late January 1900 (56). However, as their initial Chemical Society of Paris presentation (50) predated Alexander's publication, they maintained their priority of the discovery (54). Of course, it is interesting to note that they do not recognize the very similar previous report by Erdmann and Köthner (48) and it is unknown if they were aware of it or not.

### Alexander and Continued Studies of Acetylene over Copper

Little is known about Hans Alexander, other than that he worked in the electrochemical laboratory of the Royal Technical University of Berlin and published a handful of papers over the timespan of 1898-1910. Only one of these papers is pertinent to the current discussion, which he published in August of 1899 (55), three months after Sabatier presented his initial findings on cuprene at the meeting of the Chemical Society of Paris (50). He begins the paper by pointing out its relationship to the previous work of Erdmann and Köthner (48), as well as some related work by Sabatier and Senderens on the hydrogenation of acetylene over nickel. He does not seem to be aware of the report of Sabatier at the Chemical Society.

Using very similar methods to Sabatier and Sendrens (54), Alexander passed acetylene through a tube containing evenly distributed copper. At ordinary temperatures, no visible reaction was observed. However, when the acetylene-filled tube was slowly heated, a change was seen at 225°C, in which the copper began to swell, the gas flow slowed, and greenish, strong smelling droplets of hydrocarbons condensed on the colder part of the tube. If the temperature was allowed to reach 260°C, black shiny carbon crystals began to deposit on the walls of the tube. However, if the temperature was held between 240 and 250°C, the reaction proceeded smoothly to fill the whole tube with a light brown mass (55).

The material produced exhibited a non-uniform composition. The material at the entry point of the gas was found to be comprised of lightweight, odorless, dark colored flakes. The material at the other end of the tube, however, contained a strong hydrocarbon smell and a slightly darker color, but the main content of the tube consisted of a uniform, light brown mass. Analysis of the copper content of the material revealed greater copper content in the material located near the entry point of the gas, but that the bulk of the material was found to contain 2% copper (55).

Alexander reports that no solvent was found that could dissolve the material, but that some copper was removed by treating the material with dilute HCl. However, the material could not be made completely copper-free by such treatment, even after boiling the material for several hours. However, it was found that the copper could be completely removed by boiling the material in HCl containing some ferric chloride. The material treated in this way now contained trace amounts of iron, even after boiling with fresh HCl, with a final iron content of 0.2%. This nearly metal-free material looked a little brighter than the original copper-containing material, but otherwise exhibited no measurable difference (55).

As a result of these observations, Alexander disputed the previous claim by Erdmann and Köthner (31) that this material was a copper compound and believed that the copper was only mechanically mixed throughout this material. He ultimately concluded (55):

In my view, the copper serves only as a contact substance, under the influence of which a polymerization of the acetylene takes place. Here, a small amount of aromatic hydrocarbons form, which distill out, while mainly a very high molecular weight hydrocarbon of cork-like nature arises.

Following Alexander's report, but still before Sabatier's full publication, yet another related study appeared in November of 1899 (57). This study was the first report on the subject from outside Europe, coming from Frank Gooch (1852-1929) and De Forest Baldwin at Yale University in the United States.

### Gooch and Further Studies of Acetylene over Copper Oxide

Frank Austin Gooch was born on May 2, 1852, in Watertown, Massachusetts (58, 59). His formal schooling also began there, but he transferred to Mr. Atkinson's school in Cambridge (later known as the Kendall School) when he was 12 (58). He entered Harvard College in 1868, at the age of 16 (58, 59). There, he devoted himself to physics and chemistry, graduating in 1872 (39, 40) with the degree of A. B. *cum laude*, with "*summos in Physicis et Chemia honores*" (58).

Following graduation, Gooch began graduate work at Harvard, studying chemistry, physics, and mineralogy. He became an assistant to Josiah P. Cooke (1827-1894) in his second year (58, 59), while also serving as assistant in the quantitative analysis laboratory for the 1874-1875 school year (58). His training under Cooke furthered his interest in chemistry, but he was also greatly interested in the physics of crystals, and thus he spent the following year abroad in Straßburg and Vienna studying such subjects (58, 59).

He resumed his studies at Harvard in the autumn of 1876. Having completed work for his A.M. and Ph.D. degrees in early June 1877, he left again to pursue the possibility to work with Julius Thomsen (1826-1909) in Copenhagen. His time abroad, however, was short lived and he returned to Harvard to work with Wolcott Gibbs (1822-1908), which lasted for two years (58). Following this, he held a number of positions performing analytical work with the United States Tenth Census (1879-1881), the North Transcontinental Survey (1881-1884), and the United States Geological Survey (1884-1886) (59). Gooch then moved to New Haven, Connecticut, in 1886, to become Professor of Chemistry in Yale College, where he spent the rest of his career. Although his published work covered a wide range, it focused chiefly in the field of analytical chemistry. He died on August 12, 1929, in New Haven (58).

On November 4th, 1899, Gooch and his coauthor De Forest Baldwin reported (57) a continuation of the previous study by Erdmann and Köthner (48). After a

brief summary of the results of Erdmann and Köthner, they pointed out that careful examination of the analysis data revealed an error in the calculations (57). Thus, while Erdmann and Köthner had reported a formula of  $C_{44}H_{64}Cu_3$ , Gooch and Baldwin stated that the correct carbon to hydrogen ratio should be 6.45:5.70, i.e., less hydrogen than carbon rather than the inverted relationship initially published. They also expressed doubts about the copper percentages, but could not give more correct values without more detailed information (57).

In order to provide more accurate data, the authors then proceeded to perform their own study of acetylene over copper oxide under various conditions in order to determine any effects on the chemical composition of the products. As Erdmann and Köthner had observed faster reaction rates when using copper oxide compared to copper (48), Gooch was especially interested in any possible role of oxygen in the observed reactions. Depending on the conditions, copper content was found to range from 1.54-24.21% and it was found that the use of cuprous or cupric oxide gave nearly identical results.

Similar to observations reported by Sabatier (54), it was found that samples could be further heated with acetylene to restart the reaction, thus giving products with lower percentages of copper. To further study the effect of copper versus copper oxide, one end of a copper coil was oxidized in a flame. The full coil was then subjected to acetylene under heat, resulting in the formation of product only at the oxidized end while the other end simply changed color (57).

These studies revealed that the material produced in all cases was not uniform, with the bulk of the material a spongy mass of light brown color, while that material closer to the original copper source was darker in color. The material of "the brightest color" ("der hellsten Farbe") was found to contain very little copper and no oxygen, while the darkest product contained higher copper and oxygen content, with the oxygen believed to originate in the copper oxide reagent. As such, it was ultimately concluded that the product was not a copper compound and that the copper and/or copper oxide was mechanically entrapped in the hydrocarbon produced. Under the assumption that the product consisted of only carbon and hydrogen, the data was fit to give formulas ranging from  $C_{12}H_{10}$  to  $C_{16}H_{10}$ , with an average empirical formula of  $C_{14}H_{10}$  (57). Recalculating the data of Erdmann and Köthner under these same assumptions gave a formula consistent with the low end of this range, which is also consistent with the empirical formula of Sabatier and Senderens.

Not only did Gooch and Baldwin directly connect their work to that of Erdmann and Köthner (48), but they seem to be the first of those discussed so far to also connect these reactions over copper to the previous thermal polymerizations of Berthelot (18, 19). As no mention is made of either Sabatier or Alexander, it is unclear if they were aware of these additional studies. After this second flurry of studies on acetylene-based materials from 1898 to 1900, no further reports appeared until that of Sima Lozanić (1847-1935) in 1907 (60).

### **Sima Lozanić and a Return to Polymerization via Electric Discharge**

Sima M. Lozanić (Losanitsch) was born on February 24, 1847, in Belgrade, Serbia (61). He studied law at Belgrade College, after which he spent four years in Zürich and Berlin. There, he studied chemistry under Johannes Wislicenus (1835-1902) and August Wilhelm von Hofmann (1818-1892). In 1872, he joined the Department of Chemistry at Belgrade College, which became the University of Belgrade in 1905. With the transition from College to University, Lozanić was appointed the chairman of the University Board and later became the first University president (61).

The Serbian Academy of Sciences was founded in 1883 and Lozanić became a corresponding member two years later (61). He became a full member in 1890 and was twice elected the Academy's president (in 1899 and 1903). Lozanić was awarded an honorary doctorate by the University of Belgrade in 1922 and he retired in 1924, although he continued to work until 1929. He died July 7, 1935 in Belgrade, at the age of 88 (61).

In the fall of 1907, Lozanić reported a series of experiments on electrosynthesis in which various gases or gaseous mixtures were subjected to electric discharge (60). These efforts used a discharge device originally designed by Berthelot, although with a couple personal modifications. These modifications allowed him to hermetically enclose the gases in the apparatus, as well as measure the gas pressure during the experiment. Although much of the report details experiments of bimolecular mixtures of acetylene with other species ( $O_2$ ,  $CH_4$ , ethylene,  $H_2S$ ,  $CO$ , and  $SO_2$ ), he started his study of acetylene with the pure gas (60).

As with previous studies, Lozanić's efforts resulted in the generation of two products, one described as a viscous mass soluble in alcohol or ether, and the other an insoluble, strong smelling solid (60). The greater of these



two was the solid product, described as yellow-brown in reflected light and yellow-red in transmitted light. As previously reported by Berthelot (42), both products were found to decompose rapidly at temperatures over 100°C to give carbon. Otherwise, however, the products were found to be very stable, with no reaction observed upon treatment with hot, fuming nitric acid (60).

Lozanić was troubled by the results of analysis of the products, which revealed content beyond carbon and hydrogen (60). He initially assumed that this was due to an impurity in the acetylene used, but carefully purified acetylene gave similar results. He then noticed that the solid material stored in a desiccator gained mass, with this gain saturated after 26 days at ca. 10%. After eliminating nitrogen as a possibility, he concluded that this must be due to oxygen absorption (60).

Although Lozanić appeared to be familiar with the previous reports of Berthelot, he did not mention any of the other previous studies on the effects of electric discharge on acetylene, nor did he connect the products of electric discharge to those produced via thermal polymerization. Although he stated that he planned to follow up the oxygen absorption at a later date, he did not seem to do so and no further reports appeared until that of Daniel Berthelot (1865-1927) three years later in 1910 (62).

### Daniel Berthelot and UV Polymerization

Daniel Paul Alfred Berthelot was born on November 8, 1865, in Paris (63). His father was Marcellin Berthelot (63, 64), with whom the whole current account began. The younger Berthelot was educated at the Sorbonne and in the Museum at the Collège de France, his teachers including Paul-Quentin Desains (1817-1885), Henri Becquerel (1852-1908), and Gabriel Lippmann (1845-1921) (64). He was then appointed professor of physics at the École de Pharmacie of the Université de Paris (63, 64).

At the École de Pharmacie and in his laboratory of plant physics at Meudon (64), he became known for his work in physical chemistry, including contributions in pyrometry, the electrolytic nature of acids, and the physical characterization of gases. He was perhaps best known, however, for his contributions in photochemistry (63, 64). For his accomplishments, Berthelot was awarded the Jecker Prize by the Académie des Sciences in 1898 and Hughes Prize in 1906. On February 24, 1919, he was elected a member of the Académie. Berthelot died March 8, 1927, at the age of 62 (63).

In collaboration with Henri Gaudechon, Berthelot reported the photochemical polymerization of acetylene in 1910 (62). Using a quartz mercury vapor lamp (110 volts, 2.5 amps), acetylene gas was irradiated with UV light to generate a yellow solid which was reported to have the characteristic odor of acetylene polymers. No benzene was produced in the process and no other gaseous products were detected. Irradiation of mixtures of acetylene with either hydrogen or nitrogen resulted in more efficient generation of the yellow solid, with H<sub>2</sub> or N<sub>2</sub> appearing to act only as inert buffer gases and no reaction of these gases was observed (62). Finally, mixtures of acetylene and ethylene were irradiated to again give the yellow solid identical in appearance to the previous acetylene polymers, along with a greasy coating stated to be consistent with condensed ethylene.

Unfortunately, no further study of the yellow solid was reported, nor was any connection made to the many previous studies discussed above. Following the independent studies of Lozanić and Daniel Berthelot, there was another sizeable gap in related studies. Efforts ramped up again in the 1920s and 30s, however, beginning with the work of H. P. Kaufmann (1889-1971) in 1918 (65).

### Kaufmann and Comparative Studies of Electric Discharge vs. Thermal Polymerization

Hans Paul Kaufmann was born October 20, 1889, in Frankfurt, Germany (66). Starting in 1908, he studied chemistry in Jena, Heidelberg, and Berlin (66, 67), obtaining his Ph.D. under Ludwig Knorr (1859-1921) at Jena in January 1912 (66). He worked as a research assistant at Jena's Chemical Institute from 1911 to 1914, before joining the German army with the outbreak of World War I. After the delay caused by the war, he finally obtained his habilitation on May 17, 1916, while on leave from military duty (66, 67). He was seriously wounded shortly thereafter and was assigned to war-related scientific work following his recuperation (66). He became außerordentlicher Professor (Professor extraordinarius) and Director of the Analytical Division of Jena's Chemistry Institute in 1919 (66, 67).

After the early death of his mentor Knorr, he moved to Jena's Pharmaceutical Institute (66), where he began teaching in 1922 (66) after finishing the pharmaceutical state examination (67). He then moved to Münster as Professor of Pharmacy in 1931 (66, 67) and remained there until he moved to Berlin as Professor of Pharmaceutical Chemistry in 1943 (66). He returned to Münster

in 1946 to become Professor of Pharmacy and Chemical Technology. He became Professor Emeritus in 1958, although he continued as the director of the Pharmacy and Food Chemistry Institute until April 1959. After an extended illness, Kaufmann died October 2, 1971 (66).

Although best known for his work on fats and oils, he did not publish in this area until 1925 and his habilitation thesis was concerned with the polymerization of acetylene (65, 66). His habilitation research, in which he attempted to provide some clarity concerning the composition of the products generated by subjecting acetylene to electric discharge, was then published in 1918 (65). These efforts began with optimizing the reaction conditions in order to produce the products in higher yield, such that a suitable amount of material could be obtained for further study. He found that if the discharge apparatus was suitably cooled, only the liquid product was produced. Alternately, if the apparatus was poorly cooled, the solid product was favored (65, 68).

As found previously by the Thenards (31) and others, the solid product adhered rather firmly to the apparatus walls. Kaufmann, however, found that the addition of ice water caused the product to loosen from the walls as a brown, brittle mass (65). Even better, he found that if the initial oil was subjected to discharge as a heated solution, a fine, light yellow powder was produced, which exhibited all of the properties of the previous solid mass, but was more suitable for further analysis. Kaufmann then proceeded to study the treatment of this product with various reagents (65).

These efforts began with the study of oxygen absorption, originally observed by Berthelot. Kaufmann stated that although Lozanić had previously proposed that the amount of oxygen absorbed should allow calculation of the number of double bonds contained in the product (60), he disagreed as only non-cyclic double bonds would be expected to react with oxygen. He thus stated that this reactivity did not allow one to draw any conclusions about the material at present (65).

He then continued his study by treating the solid product with various reducing and oxidizing agents. Although no reactions were observed with reducing agents, heating the solid material in dilute nitric acid for prolonged periods did result in some nitrated products. Treating the solid with alkaline potassium permanganate was more successful, however, ultimately giving low amounts of benzoic, isophthalic, and terephthalic acids. He thus concluded that much of the structure consisted

of unsaturated chains, which generated carbon dioxide upon permanganate oxidation (65).

Kaufmann then followed this with two additional papers in which he compared acetylene polymerization via electric discharge to its catalyzed and non-catalyzed thermal polymerization (68) and studied the copper-catalyzed process in more detail (69). As previously noted by others, he reports that the nature of the catalyst plays a significant role, with copper bronze and copper oxides working much better than pure copper (68, 69). He then went on to show that cuprene could be successfully produced via the use of catalytic cupriferricyanide ( $\text{CuFe}(\text{CN})_6^{2-}$ ) (68), but ultimately concluded that the presence of oxygen in the process was required (69).

As previously shown by Alexander (55), the copper content could not be removed by treatment with HCl. However, he found that several hours of boiling with aqua regia did result in a material with only trace copper content (68). He then went on to analyze these products via reduction or oxidation. As with his previous study of the electric discharge products (65), reduction was unsuccessful. However, treatment of the copper-catalyzed products with 80%  $\text{HNO}_3$  gave mellitic acid (benzenehexacarboxylic acid), benzoic acid, and a naphthalene derivative as oxidation products (68). Lastly, he found that cuprene could be brominated via treatment with  $\text{Br}_2$  in the presence of iron halides, although he noted that different brominated products formed according to the exact experimental conditions (68).

These collective results led to the conclusion that cuprene is not a uniform substance, and that the term must be understood to mean a mixture of acetylenic condensation products, the composition of which was variable (69). In addition, cuprene must contain benzene units, as well as attached carbon chains that were not completely aliphatic, but yet likely not fully unsaturated either (68). It was thus felt that the unsaturation was primarily included as aromatic units (69). Within a couple years of Kaufmann's work, the Belgian Walter Mund (1892-1956) showed that acetylene could also be polymerized via the application of alpha rays (70).

### Mund and Polymerization via Alpha Particles

Walter Emile Marie Mund was born in Antwerp on January 22, 1892 (71). After attending the Jesuit College in his hometown, he enrolled as a candidate in the natural sciences at Leuven (Louvain) in October of 1910. He then

received a doctorate in natural sciences on July 24, 1914, with a dissertation entitled "On the Vapor Pressures of Sulfur Dioxide," under the direction of Pierre Bruylants (1885-1950) (71).

Unfortunately, World War I broke out only days after he completed his doctorate, thus interrupting what should have been the start of a promising academic career. In August of 1914, Louvain fell to the German First Army and was the subject of mass destruction shortly thereafter. Mund and his family were evacuated to Manchester, England, where he joined an oil company as a chemist. It is unclear whether Mund left Louvain before or after the German occupation. He left his laboratory in 1916, however, to join the Battle of the Yser first as a mere rifleman, and later a corporal. His bravery and his leadership earned him the Cross of Fire and the Medal of Victory (71).

After the war, Bruylants succeeded to the chair of general chemistry and Mund was called to lead the Physical Chemistry Laboratory at Leuven. For more than thirty years he taught physical chemistry there and distinguished himself by his researches in what would now be described as radiation chemistry, with particular emphasis on the study of chemical reactions that can be triggered by  $\alpha$  particles. He published more than 100 papers in the *Bulletin des Sociétés Chimique Belges* and his work was recognized by the government's Decennial Award of Chemistry. He died on August 15, 1956, at the age of 64 (71).

In 1925, Mund and W. Koch began studying the effect of radiation on various hydrocarbon gases, including methane, ethane, ethylene, and acetylene (70). Using radium, they treated a 40 cm<sup>3</sup> bulb of acetylene with 58 millicuries of emanation and monitored the reaction for 8 days. Within the first day, a dense fog filled the bulb with a fine yellow-brown powder depositing on the walls. Collecting the greater part of this yellow powder, they found it to be odorless, light as pollen, and with no obvious crystalline structure when examined under a microscope. In addition, the powder exhibited low solubility and no trace of fusion in sulfuric acid up to 300°C. Ultimately, it was determined that the product was a hydrocarbon with a formula that approximates that of acetylene (70) and proposed that it was identical to the material previously reported by Alexander (55).

Later that same year, they studied the effect of  $\alpha$  particles on acetylene in more detail, this time using radon as the source (72). It was determined that each  $\alpha$  particle caused the condensation of  $4.38 \times 10^6$  molecules

of acetylene, but it was admitted that not all molecules may have undergone polymerization and some molecules could have been absorbed by the resulting product. In terms of mechanism or structure, they admitted that it was not easy to establish either, but they were convinced that the material was identical to cuprene (72).

The following year, these studies were continued with a focus on the effect of oxygen, pressure, and temperature (73). However, it was determined that none of these variables had any effect on the previously determined values. Mund returned to the study of acetylene with two later papers in the 1930s (74, 75), but by then the primary study of acetylene polymerization had been continued by Samuel Lind (1879-1965) (76).

### Lind and the Continued Study of Acetylene Polymerization under Various Conditions

Samuel Lind was born in McMinnville, Tennessee, on June 15, 1879 (77). He was educated in the public schools there, before enrolling at Washington and Lee University in 1895. He spent most of his first three years studying French, Latin, Greek, German, and Anglo-Saxon. Entering his senior year, he still needed six credits in science, and was persuaded to take chemistry. Although he had little previous chemistry knowledge, he became captivated by the subject due to the influence of Jas Lewis Howe, who taught all the chemistry courses. Receiving his B.A. in 1899, Lind returned to Washington and Lee for additional chemistry courses, as well as courses in geology and mineralogy (77).

In the fall of 1902, he entered the Massachusetts Institute of Technology (MIT). Although MIT did not give graduate degrees at the time, he carried out research under the direction of Arthur Amos Noyes (1866-1936). Awarded a Dalton traveling fellowship in 1903, he decided to go to the Institut für Physikalische Chemie in Leipzig, where he began research under Max Bodenstein (1871-1942) on the kinetics of the reaction between H<sub>2</sub> and Br<sub>2</sub>. After Lind received his Ph.D. in August 1905, Bodenstein offered him an assistantship, but he decided to return to the United States where he accepted a teaching position at the University of Michigan (77).

In 1910, he spent time in the Paris laboratories of Marie Curie (1867-1934), where he gained proficiency in the handling of radioactive species. He then moved to the newly formed Institut für Radiumforschung in Vienna in 1911 to study the action of alpha particles on oxygen molecules. Such study of chemical reactions induced

by ionizing radiation was then to be his main field of research for the remainder of his career (77).

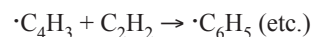
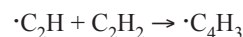
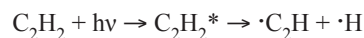
Lind accepted an appointment with the U.S. Bureau of Mines in 1913, where he worked on the extraction of radium from carnotite. He remained there until 1925, when he became assistant director of the Fixed Nitrogen Research Laboratory of the U.S. Department of Agriculture. He did not stay long, however, and became the head of the University of Minnesota's School of Chemistry in 1926, where he remained until his retirement in 1947. He became a consultant to the Union Carbide Corporation in 1948 and then served as acting director of Oak Ridge National Laboratory's chemistry division for several years. He died on February 12, 1965, while fishing below Norris Dam in Tennessee (77).

Lind began studying the effect of ionizing radiation on ethane in 1924, before extending this to additional organic gases the following year (76). In his late 1925 paper, Lind confirmed the previous report of Mund and Koch (70) as well as expanding the study to additional gases. The following year, Lind focused these studies on the more complex unsaturated gases acetylene, cyanogen, HCN, and ethylene (78). Here, he again confirmed that the treatment of acetylene with  $\alpha$  radiation resulted in a light yellow powder, which he stated was similar to cuprene via copper-catalyzed reactions or related materials produced via UV light or electric discharge (78). For the most part, his acetylene results were very similar to that of Mund and Koch (70).

To compare the polymerization of acetylene via  $\alpha$  particles to that of UV light, Lind then carried out detailed studies of the parameters of UV-induced polymerization in a 1930 communication (79). He found that wavelengths shorter than 253.7 nm were required to induce polymerization, most likely due to the transparency of acetylene at longer wavelengths. After studying the rate under various conditions, he proposed that the polymerization rate was proportional to the intensity of absorbed light but is otherwise independent of the acetylene pressure. Lastly, he determined a quantum yield of  $7.4 \pm 2.5$  for the photo-induced reaction (79). He then followed this with a full paper in 1932 (80), which provided more details, but came to all of the same conclusions. This second report did provide a more accurate determination of the quantum yield, however, with a value of  $9.2 \pm 1.5$ .

Lind returned to the photochemical polymerization one last time in 1934 (81), primarily to further refine the quantum yield to account for the additional generation of ethylene and ethane as byproducts. Thus, the total quan-

tum yield for all photochemical processes was estimated to be 9.7. More importantly, however, he also proposed the following radical mechanism for the reaction:



Lind also attempted to study the polymerization of acetylene by electric discharge in 1931, with emphasis on the reaction rate and potential insight into the reaction mechanism (82). However, no firm conclusions could be made and it was determined that further analytical data were required. Lind's final paper on acetylene polymers was a 1937 study of the oxygen-induced oxidation of cuprene samples generated via  $\alpha$  radiation (83).

### What Exactly Is Cuprene?

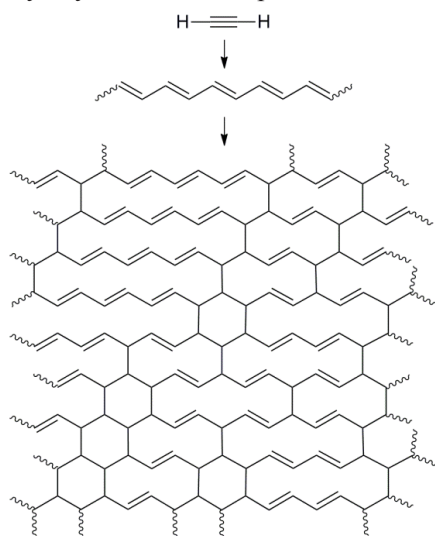
By the early 1920s, it was clear that cuprene was not a copper-based species. As noted by Kaufmann, however, the name cuprene was to be retained even though it had been shown to be a hydrocarbon (68). In addition, it was now being recognized that all of the various polymerization methods described above were producing either the same or nearly the same material, with an empirical formula very close to that of acetylene (42, 54, 57). Still, the structure of this material was unknown.

Following the mechanism proposed by Lind (81), the product should essentially be what we now recognize as polyacetylene,  $(\text{HC}=\text{CH})_n$ . In fact, this was believed to be the structure at some point, with even such polymer luminaries as Paul Flory (1910-1985) reporting its structure as such (84). However, such a structure is not consistent with the results of Kaufmann (65, 68, 69), nor was the color of cuprene consistent with polyenes longer than 4-9 repeat units (13, 17). Yet, Lind believed cuprene to exist in repeat lengths of ca. 20 (81). Of course, the report of substantiated polyacetylene by Natta in 1958 (11, 12) then finally confirmed that this was most certainly not the structure of cuprene.

A solution was then proposed in 1964, with a report that polyacetylene could be converted to a cuprene-like material by heating under  $\text{O}_2$  at temperatures above  $200^\circ\text{C}$  (85). Thus it was proposed that cuprene is formed via the initial polymerization of acetylene into linear polyenes, which were then converted to the final product by the action of residual  $\text{O}_2$ . This was then further reinforced by an additional 1971 report (86) that supported

a mechanism in which acetylene underwent primary polymerization to give linear polyenes, followed by a rapid secondary polymerization of these polyenes, and ultimately condensation and crosslinking to lead to the final intractable solid cuprene. A simplified representation of this process is illustrated in Figure 8. However, it should be stressed that cuprene's intractability, coupled with its potential structural complexity, has made a detailed determination of this structure difficult. As such, there is still much that is unknown about both its true structure and the full mechanistic details of its formation.

A product resulting from the currently accepted mechanism given above would then consist of both saturated and unsaturated sections, with the unsaturated sections consisting of relatively low conjugation length to give the material its yellow color. This species could then be viewed as a heavily crosslinked polyacetylene. However, as the crosslinking removes points of unsaturation, this perhaps more closely resembles a crosslinked polyethylene with some added points of unsaturation. This latter view is of some historical interest as cross-linked polyethylene was not reported until 1953 (87).



**Figure 8.** Simplified representation of the proposed formation of cuprene.

### Conclusion

The polymerization of acetylene to generate a light yellow, intractable material that later came to be known as cuprene dates back to 1866. Following the initial non-catalyzed thermal polymerization in 1866, it was shown that this material could be generated from acetylene by electric discharge, copper-catalyzed thermal polymerization, UV photopolymerization, and ionizing radiation ( $\alpha$

particles) from radium or radon. These polymerization studies consisted of a large number of reports over the time span of 1866-1937, after which the number and frequency of papers rapidly declined. To date, however, the detailed history of cuprene has been limited due to the disconnected nature of many of the studies of this material. At least some of this was due to the fact that prior to the work of Kaufmann in the 1920s, it was not generally recognized that these various methods were generating the same material. As a result, this produced multiple intertwined historic paths rather than a single linear narrative.

The initial interest in this material was largely due to the fact that acetylene was one of the more reactive gases known at the time and one of the only such gases that could generate a solid material other than simple carbon, which was quite remarkable in the formative period before the introduction of the modern macromolecule. The unknown nature of this solid product then continued to generate interest from continuing generations of researchers who attempted to reveal its ultimate nature. Although cuprene never developed into a commercially useful polymer, it is clearly a well-studied, early example of a synthetic polymeric material that deserves to be included in the history of polymer science along with contemporary synthetic materials such as polystyrene and polyethylene.

### Acknowledgements

I would like to thank Vera V. Mainz (University of Illinois) and Elsa B. Atson (Chemical Heritage Foundation) for assistance with tracking down sources on Paul and Armand Thenard, as well as my brother, Kent A. Rasmussen, for continued assistance with translations. Lastly, I would like to thank the Department of Chemistry and Biochemistry of North Dakota State University (NDSU) for continued support of my historical research, as well as the NDSU Interlibrary Loan Department, who went out of their way to track down many elusive and somewhat obscure sources.

### References and Notes

1. H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, "Synthesis of Electrically Conducting Organic Polymers: Halogen Derivatives of Polyacetylene,  $(CH)_x$ ," *Chem. Soc., Chem. Commun.*, **1977**, 578-580.
2. C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, B. J. Louis, S. C. Gau, and A. G. MacDiarmid,

- mid, "Electrical Conductivity in Doped Polyacetylene," *Phys. Rev. Lett.*, **1977**, *39*, 1098-1101.
3. C. K. Chiang, M. A. Drury, S. C. Gau, A. J. Heeger, E. J. Louis, A. G. MacDiarmid, Y. W. Park, and H. Shirakawa, "Synthesis of Highly Conducting Films of Derivatives of Polyacetylene,  $(CH)_x$ ," *J. Am. Chem. Soc.*, **1978**, *100*, 1013-1015.
  4. C. K. Chiang, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, and A. G. MacDiarmid, "Conducting Polymers: Halogen Doped Polyacetylene," *J. Chem. Phys.*, **1978**, *69*, 5098.
  5. N. Hall, "Twenty-five Years of Conducting Polymers," *Chem. Commun.*, **2003**, 1-4.
  6. S. C. Rasmussen, "Electrically Conducting Plastics: Revising the History of Conjugated Organic Polymers," in E. T. Strom and S. C. Rasmussen, Eds., *100+ Years of Plastics. Leo Baekeland and Beyond*, ACS Symposium Series 1080, American Chemical Society, Washington, DC, 2011, pp 147-163.
  7. S. C. Rasmussen, "The Path to Conductive Polyacetylene," *Bull. Hist. Chem.*, **2014**, *39*, 64-72.
  8. S. C. Rasmussen, "Early History of Conductive Organic Polymers," in Z. Zhang, M. Rouabhia, and S. Moulton, Eds., *Conductive Polymers: Electrical Interactions in Cell Biology and Medicine*, CRC Press, Boca Raton, FL, 2017, Ch. 1.
  9. S. C. Rasmussen, "Early History of Polypyrrole: The First Conducting Organic Polymer," *Bull. Hist. Chem.*, **2015**, *40*, 45-55.
  10. Press Release: The 2000 Nobel Prize in Chemistry, [http://www.nobelprize.org/nobel\\_prizes/chemistry/laureates/2000/press.html](http://www.nobelprize.org/nobel_prizes/chemistry/laureates/2000/press.html) (accessed July 14, 2016).
  11. G. Natta, P. Pino, and G. Mazzanti, "Polimeri ad elevato peso molecolare degli idrocarburi acetilenici e procedimento per la loro preparazione," Italian Patent 530,753 (July 15, 1955), *Chem. Abstr.*, **1958**, *52*, 15128b.
  12. G. Natta, G. Mazzanti, and P. Corradini, "Polimerizzazione stereospecifica dell'acetilene," *Atti Accad. Naz. Lincei, Rend., Cl. Sci. Fis., Mat. Nat.* **1958**, *25*, 3-12.
  13. R. Kuhn and A. Winterstein, "Über konjugierte Doppelbindungen I. Synthese von Diphenyl-polyenen," *Helv. Chim. Acta*, **1928**, *11*, 87-116.
  14. R. Kuhn and A. Winterstein, "Über konjugierte Doppelbindungen II. Synthese von Biphenyl-polyenen," *Helv. Chim. Acta*, **1928**, *11*, 116-122.
  15. R. Kuhn and A. Winterstein, "Über konjugierte Doppelbindungen III. Wasserstoff- und Bromanlagerung an Polyene," *Helv. Chim. Acta*, **1928**, *11*, 123-144.
  16. R. Kuhn and A. Winterstein, "Über konjugierte Doppelbindungen IV. Molekelverbindungen und Farbreaktionen der Polyene," *Helv. Chim. Acta*, **1928**, *11*, 144-151.
  17. N. S. Bayliss, "A 'Metallic' Model for the Spectra of Conjugated Polyenes," *J. Chem. Phys.*, **1948**, *16*, 287-292.
  18. M. Berthelot, "Action de la chaleur sur quelques carbures d'hydrogène. (Première partie)," *C. R. Acad. Sci. Paris*, **1866**, *62*, 905-910.
  19. M. Berthelot, "Les polymères de l'acétylène. Première partie: synthèse de la benzine," *C. R. Acad. Sci. Paris*, **1866**, *63*, 479-484.
  20. W. Herzog, "Über das Cupren (Carben), das technisch bedeutendste Produkt der pyrogenen Acetylenkondensation. I.," *Chem. Zeit.*, **1931**, *55*, 461-462.
  21. W. Herzog, "Über das Cupren (Carben), das technisch bedeutendste Produkt der pyrogenen Acetylenkondensation. II.," *Chem. Zeit.*, **1931**, *55*, 478-479.
  22. J. M. Calhoun, "A Study of Cuprene Formation," *Can. J. Res.*, **1937**, *15b*, 208-223.
  23. J.-P. Adloff and G. B. Kauffman, "Marcellin Berthelot (1827-1907), Chemist, Historian, Philosopher, and Statesman: A Retrospective View on the Centenary of His Death," *Chem. Educ.*, **2007**, *12*, 195-206.
  24. J. R. Partington, *A History of Chemistry*, Martino Publishing, Mansfield Centre, CT, 1998, Vol. 4, pp 465-470.
  25. M. Berthelot, "Sur une nouvelle série de composés organiques, le quadricarbone d'hydrogène et ses dérivés," *C. R. Acad. Sci. Paris*, **1860**, *50*, 805-808.
  26. Acetylene was not actually a new gas and had been originally discovered by Edmund Davy (1785-1857) in 1836 (24). Davy had never really followed up his discovery, however, and Berthelot's rediscovery of the gas in 1860 marked the beginning of its significant study and application. Berthelot was not aware of Davy's earlier discovery in 1860, but did recognize it in a 1863 review of this research on acetylene (27).
  27. M. Berthelot, "Recherches sur l'acétylène," *Ann. Chim.*, **1863**, *67*, 52-77.
  28. M. Berthelot, "Synthèse de l'acétylène par la combinaison directe du carbone avec l'hydrogène," *C. R. Acad. Sci. Paris*, **1862**, *54*, 640-644.
  29. H. Morawetz, *Polymers: The Origins and Growth of a Science*. John Wiley & Sons, New York, 1985, pp 90-91.
  30. G. Patterson, *A Prehistory of Polymer Science*, Springer Briefs in History of Chemistry, Springer, Heidelberg, 2012, p 12.
  31. P. Thenard and A. Thenard, "Acétylène liquéfié et solidifié sous l'influence de l'effluve électrique," *C. R. Acad. Sci. Paris*, **1874**, *78*, 219.

32. The family name is given by many sources as Thénard. Partington, however, explicitly states the name should not be accented (see Ref. 24, p 90) and it is not accented in the papers of Paul and Arnould Thenard.
33. B. W. Feddersen and A. J. von Oettingen, Eds, *J. C. Poggendorff's Biographisch-Literarisches Handwörterbuch zur Geschichte der Exacten Wissenschaften*, Vol. 3, J. A. Barth, Leipzig, 1898, p 1334.
34. M. Liébaud, "Une famille d'illustres savants: quelques souvenirs de Conté, Humblot-Conté, Jacques, Paul et Arnold Thenard," *Bull. Soc. Encour. Ind. Natl.*, **1907**, 106, 675-698.
35. G. Bouchard, "Avant-propos," in P. Thenard, *Un Grand Français: Le Chimiste Thenard, 1777-1857*, Imprimerie Jobard, Dijon, 1950, pp 5-8.
36. G. Vapereau, *Dictionnaire Universel des Contemporains: Contenant Toutes les Personnes Notables de la France et des Pays Étrangers*, 5th ed., Hachette, Paris, 1880, pp 1731-1732.
37. Anonymous, "Science Gossip," *The Athenaeum*, **1884**, 2966 (Aug. 30), 282.
38. J. Wisniak, "Louis-Jacques Thenard," *Revista CENIC Ciencias Químicas*, **2002**, 33, 141-149.
39. P. Thenard and A. Thenard, "Sur les combinaisons formées sous l'influence de l'effluve électrique par le gaz des marais et l'acide carbonique d'une part, et l'oxyde de carbone et l'hydrogène d'autre part," *C. R. Acad. Sci. Paris*, **1873**, 76, 1048-1051.
40. P. Thenard and A. Thenard, "Nouvelles recherches sur l'effluve électrique," *C. R. Acad. Sci. Paris*, **1873**, 76, 1508-1514.
41. M. P. v. Wilde, "Vermischte Mittheilungen," *Ber. Dtsch. Chem. Ges.*, **1874**, 7, 352-357.
42. M. Berthelot, "Quatrième mémoire. Absorption de l'hydrogène libre par l'influence de l'effluve," *Ann. Chim. Phys.*, **1877**, 10, 66-69.
43. Additional confusion relating to De Wilde's name comes from the fact that it is given inconsistently, with different sources giving it as "P. De Wilde" (44-46), "P. de Wilde" (47), or "M. P. v. Wilde" (41). In this last case, it appears that the honorific title "M." (for Monsieur in French or Meneer in Dutch) was mistaken as an initial by the German publication.
44. P. De Wilde, "Sur la production de l'acétylène. —Nouvelles méthodes," *Bull. Acad. R. Belg.*, **1865**, 19[ser 2], 12-15.
45. P. De Wilde, "Sur la production de l'acétylène. —Nouvelles méthodes," *Bull. Acad. R. Belg.*, **1865**, 19[ser 2], 91-94.
46. C. Bulens, Ed., *L'Institute Agricole de L'Etat a Gembloux, 1860-1910*, Imprimerie Scientifique, Brussels, 1910, pp 79, 101-102, 111-112.
47. C. Bulens, Ed., *The Government Agricultural Institute of Gembloux*, Imprimerie Scientifique, Brussels, 1904, pp 7-18, 27-30.
48. H. Erdmann and P. Köthner, "Einige Beobachtungen über Acetylen und dessen Derivate," *Z. Anorg. Chem.*, **1898**, 18, 48-58.
49. G. Lockemann, "Erdmann, Hugo Wilhelm Traugott," in *Neue Deutsche Biographie*, Duncker & Humblot, Berlin, 1959, Vol. 4, p 572.
50. M. Hanriot, "Extrait des Procès-verbaux des séances," *Bull. Soc. Chim. Fr.*, **1899**, 21, 529-531.
51. E. K. Rideal, "Paul Sabatier, 1859-1941," *Biogr. Mem. Fellows R. Soc.*, **1942**, 4, 63-66.
52. H. S. Taylor, "Paul Sabatier, 1859-1941," *J. Am. Chem. Soc.*, **1944**, 66, 1615-1617.
53. A. G. Morachevskii, "Paul Sabatier (to 150th Anniversary of His Birthday)," *Russ. J. Appl. Chem.*, **2004**, 77, 1909-1912.
54. P. Sabatier and J. B. Senderens, "Action du cuivre sur l'acétylène: formation d'un hydrocarbure très condensé, le cuprène," *C. R. Acad. Sci. Paris*, **1900**, 130, 250-252.
55. H. Alexander, "Ueber die Einwirkung des Acetylens auf Kupfer," *Ber. Dtsch. Chem. Ges.*, **1899**, 32, 2381-2384.
56. V. Auger, "Action de l'acétylène sur le cuivre: Hans Alexander," *Bull. Soc. Chim.*, **1900**, 24, 38.
57. F. A. Gooch und D. F. Baldwin, "Die Einwirkung von Acetylen auf die Oxyde des Kupfers," *Z. Anorg. Chem.*, **1899**, 22, 235-240.
58. R. G. Van Name, "Frank Austin Gooch," *Biogr. Mem. Nat. Acad. Sci. USA*, **1931**, 15, 105-135.
59. P. E. Browning, "Frank Austin Gooch," *Ind. Eng. Chem.*, **1923**, 15, 1088-1089.
60. S. M. Losanitsch, "Über die Elektrosynthesen. II," *Ber. Dtsch. Chem. Ges.*, **1907**, 40, 4656-4666.
61. B. Snežana, "Sima Lozanić (1847-1935)," in V. D. Djordjević, D. Vitorović, and D. Marinković, Eds, *Lives and Work of Serbian Scientists*, Serbian Academy of Sciences and Arts, Belgrade, 2006, pp 153-155.
62. D. Berthelot and H. Gaudechon, "Effets chimiques des rayons ultraviolets sur les corps gazeux. Actions de polymérisation," *C. R. Acad. Sci. Paris*, **1910**, 150, 1169-1172.
63. J. Wisniak, "Daniel Berthelot. Part I. Contribution to Thermodynamics," *Educ. quim.*, **2010**, 21, 155-162.
64. C. Barrois, "Mémoires et Communications des Membres et des Correspondants de l'Académie," *C. R. Acad. Sci. Paris*, **1927**, 184, 637-641.

65. H. P. Kaufmann, "Über die Produkte der Einwirkung der dunklen elektrischen Entladung auf Acetylen," *Ann. Chem.*, **1918**, 417, 34-59.
66. G. Knothe, "Giants of the Past. Hans Paul Kaufmann (1889-1971)," *Inform*, **2004**, 15, 802-803.
67. K. Täufel, "Professor Dr. Dr. h. c. H. P. Kaufmann," *Nahrung*, **1959**, 3, 789-792.
68. H. P. Kaufmann and M. Schneider, "Acetylen-Kondensationen, I.: Versuche zur Konstitutionsermittlung des Cuprens," *Ber. Dtsch. Chem. Ges.*, **1922**, 55, 267-282.
69. H. P. Kaufmann and W. Mohnhaupt, "Zur Theorie der Bildung des Cuprens (Acetylen-Kondensationen, II.)," *Ber. Dtsch. Chem. Ges.*, **1923**, 56, 2533-2536.
70. W. Mund and W. Koch, "Sur l'altération chimique de quelques hydrocarbures gazeux sous l'action du rayonnement radioactif," *Bull. Soc. Chim. Belg.*, **1925**, 34, 119-126.
71. R. Belche, "A la mémoire de Walter Mund," *Inst. Grand-Ducal Luxembourg, Sect. sci., nat., phys. et math., Arch.*, **1956**, 23, 23-25.
72. W. Mund and W. Koch, "Sur la polymérisation de l'acétylène sous l'action des particules  $\alpha$ ," *Bull. Soc. Chim. Belg.*, **1925**, 34, 241-255.
73. W. Mund and W. Koch, "The Chemical Action of  $\alpha$  Particles on Acetylene," *J. Phys. Chem.*, **1926**, 30, 289-293.
74. W. Mund, "The Insert Gas Effect in the Radiochemical Polymerization of Acetylene," *J. Phys. Chem.*, **1934**, 38, 635-637.
75. W. Mund, "The Formation of Benzene in the Radiochemical Polymerization of Acetylene," *J. Phys. Chem.*, **1937**, 41, 469-475.
76. S. C. Lind and D. C. Bardwell, "The Chemical Effects in Ionized Organic Gases," *Science*, **1925**, 62, 422-424.
77. K. J. Laidler, "Samuel Colville Lind," *Biogr. Mem. Natl. Acad. Sci. USA*, **1998**, 74, 227-242.
78. S. C. Lind, D. C. Bardwell, and J. H. Perry, "The Chemical Action of Gaseous Ions Produced by Alpha Particles VII. Unsaturated Carbon Compounds," *J. Am. Chem. Soc.*, **1926**, 48, 1556-1575.
79. S. C. Lind and R. S. Livingston, "The Photochemical Polymerization of Acetylene," *J. Am. Chem. Soc.*, **1930**, 52, 4613-4614.
80. S. C. Lind and R. S. Livingston, "The Photochemical Polymerization of Acetylene," *J. Am. Chem. Soc.*, **1932**, 54, 94-106.
81. S. C. Lind and R. Livingston, "The Photochemical Polymerization of Acetylene," *J. Am. Chem. Soc.*, **1934**, 56, 1550-1551.
82. S. C. Lind and G. R. Schultze, "The Condensation of Hydrocarbons by Electrical Discharge. VIII. The Condensation as a Function of Time and Pressure," *J. Am. Chem. Soc.*, **1931**, 53, 3355-3366.
83. S. C. Lind and C. H. Schifle, "Studies in the Oxidation of Alpha Ray Cuprene," *J. Am. Chem. Soc.*, **1937**, 59, 411-413.
84. P. J. Flory, "The Heat of Combustion and Structure of Cuprene," *J. Am. Chem. Soc.*, **1937**, 59, 1149-1150.
85. R. J. Fredericks, D. G. Lynch, and W. E. Daniels, "Thermal Properties of Polyacetylene: on the Origin of Cuprene in Reppe's Cyclooctatetraene Synthesis," *J. Polym. Sci., Part B: Polym. Lett.*, **1964**, 2, 803-808.
86. J. P. Briggs and R. A. Back, "The Effect of Electric Fields on the Radiolysis of Acetylene, and the Mechanism of Cuprene Formation," *Can. J. Chem.*, **1971**, 49, 3789-3794.
87. H. Morawetz, *Polymers: The Origins and Growth of a Science*, John Wiley & Sons, New York, 1985, pp 180-181.

### About the Author

Seth C. Rasmussen is Professor of Chemistry at North Dakota State University (NDSU) in Fargo. He received a B.S in Chemistry from Washington State University in 1990 and a Ph.D. in Inorganic Chemistry from Clemson University in 1994, under the guidance of Prof. John D. Petersen. In 1995, he then studied conjugated organic polymers under Prof. James E. Hutchison as a postdoctoral associate at the University of Oregon. In 1997, he accepted a teaching position at the University of Oregon, before moving to join the faculty at NDSU in 1999. Active in the fields of materials chemistry and the history of chemistry, his research interests include the design and synthesis of conjugated materials, photovoltaics (solar cells), organic light emitting diodes, the history of materials, chemical technology in antiquity, and the application of history to chemical education. Prof. Rasmussen currently serves as the Program Chair for the ACS Division of the History of Chemistry and as Series Editor for *Springer Briefs in Molecular Science: History of Chemistry*, as well as holding editorial positions for the journals *Cogent Chemistry*, *Fluorescent Materials*, and *Topological and Supramolecular Polymer Science*.