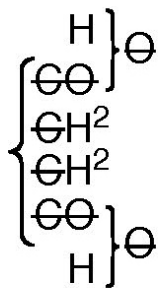Butlerov

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Reconciling Ideas on Organic Structure

BULLETIN FOR THE HISTORY OF CHEMISTRY
VOLUME 40 CONTENTS

NUMBER 1

REDISCOVERING PYROTARTARIC ACID: A CHEMICAL INTERPRETATION OF THE VOLATILE SALT OF TARTAR

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Abstract

Pyrolysis, the action of heat on organic substances in anaerobic conditions, has been one of the earliest not only analytical but also synthetic methods both in alchemy and chemistry. Applied to carboxylic acids this process allowed the preparation of a variety of chemicals, of which acetone is the best known example. But the nature of a product obtained from tartar, the *volatile salt of tartar*, generated a great deal of controversy among practitioners of alchemy because of its claimed involvement in the preparation of Paracelsus' *alkahest*. In this article the identification of volatile salt of tartar with pyrotartaric acid is suggested, by tracing the most relevant studies on the pyrolysis of tartar from alchemy to modern chemistry.

Introduction

The conversion of carboxylic acids to ketones, also called ketonic decarboxylation, is a useful chemical transformation that allows the production of symmetrical ketones. In this process, two carboxylic acid functionalities are converted into a carbonyl group with elimination of carbon dioxide and water (Scheme **1**) (1). α- and β-ketoacids as well can undergo either thermal or enzymatic decarboxylation to yield ketones. Despite being one of the oldest reactions known in organic chemistry, it has very promising industrial applications because the

reactants are cheap, the by-products are innocuous and it doesn't require any solvent.

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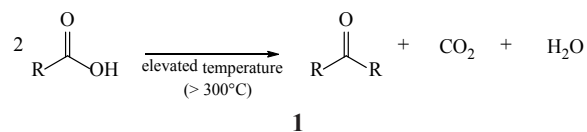
In this context, tartaric acid is a case of particular interest: subjected to pyrolysis, it gives two products, namely pyrotartaric acid and pyruvic acid (Scheme **2**).

Tartaric acid Pyrotartaric acid (methylsuccinic acid) Pyruvic acid

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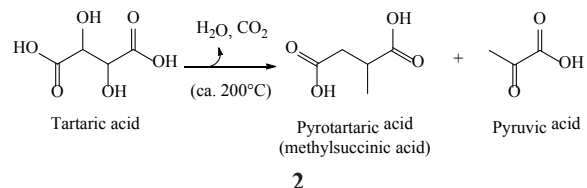
Although the history of the preparation of acetone by ketonic decarboxylation has been well documented since the first report in 1612 by Jean Beguin and is in fact common knowledge (2), that of pyrotartaric acid and pyruvic acid is not. This is rather confusing since the studies on the pyrolysis of tartar (the natural source of tartaric acid) and of the obtained products not only attracted the alchemists' attention earlier but were also taken into greater consideration because of their applications in medicine and in alchemical operations. Alchemists and Paracelsian iatrochemists claimed that it was possible to

extract a *volatile salt* from tartar, whose chemical nature remained controversial. The first detailed procedure for the preparation of this substance appeared in 1675 in Nicholas Lémery's *Cours de Chimie* (3).

The aim of the present article is to review the most relevant studies on the pyrolysis of tartar, starting from alchemy to modern organic chemistry, to suggest the identification of Lémery's volatile salt of tartar with pyrotartaric acid.

The Alchemy Period

Tartar is a saline concretion that wine naturally produces during storage in casks. The formation of tartar during vinification has been known since ancient times: it was initially called *faex vini*, and the word *tartarus* began to appear in the alchemical literature of the eleventh century (4, 5).

This body was the subject of intense research because the alchemists were attracted by its double nature, both vegetable and mineral. Tartar was early recognized as a valid source of useful chemicals: the first to be obtained were *cremor tartari*, which is tartar purified by crystallization from a saturated aqueous solution and *sal tartari*, an alkaline substance obtained by the calcination of tartar in open air. A variety of other derivatives have been described, such as the *tartarus emeticus* reported by Adrien von Mynsicht in 1631 (6) and the *Rochelle salt* prepared by Pierre Seignette around 1660 (7). Both were used in medicine, the first as an emetic and the latter as a purgative. Chemically speaking, *cremor tartari* is the monobasic potassium salt of tartaric acid or potassium bitartrate; by calcination in open air it is converted into potassium carbonate, which is a deliquescent alkaline solid melting at 891°C. *Tartarus emeticus* is an antimony potassium tartrate and *Rochelle salt* is a sodium potassium tartrate.

The uses of tartar spanned from pharmacy to metallurgy, where *fluxum nigrum*, obtained by partial calcination of tartar, was employed as a melting and (due to its high carbon content) reducing agent. By heating tartar with potassium nitrate—a process known as *detonation*—another kind of flux, *fluxum album*, could be obtained. *Fluxum nigrum* is a mixture of potassium carbonate and carbonized organic matter while *fluxum album* is potassium carbonate. The ability of tartar to increase the malleability of metals led to the belief that powerful agents for the transmutation of metals could be extracted from it. This is how the alchemist Johannes

de Monte-Snyder (~1625-1670) explained the effect of tartar on the melting of metals (8):

> As the spirit of wine is known to be a sublime solvent and medicine, likewise tartar is not to be disregarded. Its spirit can be used for the unclogging of metals, thereby increasing their malleability and therefore also their salt; the malleability of metals depends in fact on the salt and any method by which they are made malleable acts by increasing the salt content. ... Tartar improves metals and makes them more malleable, joining them in the metallic salts formed from compounding with tartar. The malleability of metals resides in the abundance of salt, so if by the aid of Tartar a metal becomes more malleable at the same time the metallic salt must have increased. By means of Tartar the metals are changed into living Mercury, and this happens because while quantitatively the salt is increased, the Earth begins to predominate until the bond is broken. Indeed, when Earth increases, the Spirit which is not extensive but intensive is forced to expand excessively, causing dissociation and visibly contracting itself into quicksilver. [author's translation]

It should be noted here that according to the Paracelsian doctrine of *tria prima*, all bodies (including metals) are made of three substances or *principles* (*Mercury*, the principle of fusibility, volatility, malleability; *Sulfur*, the principle of color and combustibility; *Salt*, the principle of fixity) combined in different proportions.

In the words of de Monte-Snyder there is a strong echo of an alchemical treatise, *Duodecim Claves Philosophiae*, attributed to Basilius Valentinus (9):

> In fact, the spirit of the salt of tartar, extracted per se, without additives, by solution and putrefaction, makes all metals volatile and reduces them to real living or fluent mercury, as is proven by my doctrines and practices. [author's translation]

Valentinus stated also that, if mixed with the spirit of common salt, this *spirit of tartar* can dissolve and volatilize silver and gold. It is important to state that in alchemy the term *spirit* was used to indicate volatile substances that could be sublimed and/or distilled. This led to a huge amount of work in order to obtain such a powerful solvent. Paracelsus (1493-1541) devised the word *alkahest* to describe a solvent capable of resolving a compound body into its constituent principles without being consumed or altered in the process (10).

Figure 1. *From Valentinus' treatise* Duodecim Claves Philosophiae *(9): the twelfth key is an allegory of a metallurgical operation. Note the barrel on the left.*

One of the most distinguished followers of Paracelsus, Jean Baptiste van Helmont (1579-1644), stated the possibility offered by the volatilization of the salt of tartar to obtain a powerful solvent, although not as universal as the alkahest (10):

> If you cannot attain this arcanum of fire [i.e., the alkahest], learn then to make salt of tartar volatile and complete your dissolutions by means of it.

Following this claim an incredible number of procedures to obtain such a volatile salt of tartar were proposed, which can be divided basically into two categories. The first ones were based on the controlled action of heat on tartar in accordance with the precepts of Valentinus, while the second ones tried to induce volatility in the salt of tartar by repeated distillation with volatile spirits like spirit of wine, spirit of vinegar, sal ammoniac (10). To this latter category belongs the efforts of iatrochemists like Franciscus Sylvius (1614-1672) (11) and George Starkey (1628-1665) (12) who both obtained relevant results in studying the interaction of *sal tartari* with essential oils. In such a climate of passionate and disordered research, as the alchemist Blaise De Vigenère (1523-1596) wrote, tartar became "one of the subjects which those who experiment with fire greatly abuse" (13).

Nicholas Lémery's Volatile Salt of Tartar

In 1675 the iatrochemist Nicolas Lémery (1645-1715) published his famous *Cours de chimie*, the first attempt to make the operation of chemistry and especially the preparation of medicinal compounds easy to understand and to execute. His intention was to describe each operation first as a simple recipe and only afterwards present a mechanical explanation for it. Lémery was the first not only to report a detailed description of the action of heat and fire on tartar but also to clearly state the extraction of a *volatile salt* from tartar by means of dry distillation (14):

> This Operation is the Salt of the Lees of Wine, volatilized by Fermentation.
>
> Dry the Lees of Wine with a gentle Fire, and fill with them two thirds of a large earthen or glass Retort, place this Retort in a Reverberatory Furnace [(15)], and fitting to it a large Receiver, give a small Fire to it to heat the Retort by Degrees, and to drive forth an insipid Phlegm, and luting carefully the Junctures of your Vessels, quicken the Fire by little and little, until you find the Receiver filled with white Clouds; continue it in this Condition, and when you perceive the Receiver to cool, raise the Fire to the utmost Extremity, and continue it so until there rise no more Vapours. When the Vessels are cold, unlute the Receiver, and shaking it about to make the volatile Salt which sticks to it fall to the Bottom, pour it all into a Bolt-head [that is, a distillation flask], fit to it a [distillation] Head with a small Receiver; lute well the Junctures, and placing it in Sand, give a little Fire under it, and the volatile Salt will rise, and stick to the [distillation] Head and the Top of the Bolt-head; take off your [distillation] Head, and set on another in its Place: gather your Salt and stop it up quickly, for it easily dissolves into a Liquor; continue the Fire, and take Care to gather the Salt according as you see it appear; but when there rises no more Salt, a Liquor will distill, of which you must draw about three Ounces and then put out the Fire.
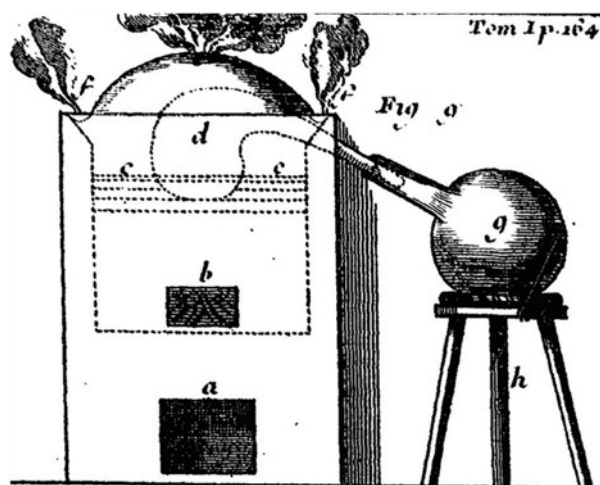

Figure 2. *Reverberatory furnace for pyrolysis experiments (16).*

Lémery described three principal products from the distillation of tartar: a *tasteless phlegm,* which in

the alchemical speech indicates a watery distillation, a white *volatile salt* and an unidentified *liquor*. In another work on this subject he reacted *cremor tartari* with the alkaline *sal tartari* obtaining *soluble tartar* (a neutral potassium tartrate), in this way demonstrating the presence in tartar of an acid. Nevertheless, a clear distinction between the acid of vinegar and the acid of tartar had not been made until the first decades of the 1700s. Even the great iatrochemist Hermann Boerhaave (1668-1738) considered this two acids to be identical; otherwise he would not have considered potassium acetate, obtained by saturating distilled vinegar with *sal tartari*, as *regenerated tartar* (17). The existence in tartar of a peculiar acid different from acetic acid was definitely recognized by Carl Wilhelm Scheele (1742-1786) in 1769, who isolated tartaric acid.

More than a century after Lémery, the chemist Pierre-Joseph Macquer (1718-1784), published another description of the analysis of tartar by pyrolysis (18):

Tartar analyzed by distillation. The Spirit, Oil, and Alkaline Salt of Tartar.

Into a stone retort, or a glass one coated with lute, put some white Tartar broken into small bits; observing that one half, or at least a full third, of the vessel be empty. Set your retort in a reverberating furnace. Fit on a large ballon, having a small hole drilled in it; lute it exactly with fat lute, and secure the joint with a linen cloth smeared with lute made of quick-lime and the white of an egg. Apply at first an exceeding gentle heat, which will raise a limpid, sourish, pungent water, having but little smell, and a bitterish taste.

When this first phlegm ceases to come off, increase your fire a little, and make the degree of heat nearly equal to that of boiling water. A thin, limpid Oil will rise, accompanied with white vapours, and with a prodigious quantity of air, which will issue out with such impetuosity, that if you do not open the little hole in the receiver time enough to give it vent, it will burst the vessels with explosion. An acid liquor will rise at the same time. Continue the distillation, increasing the heat by insensible degrees, and frequently unstopping the little hole of the receiver, till the elastic vapours cease to issue, and the oil to distill.

Then raise your fire more boldly. The acid Spirit will continue to rise, and will be accompanied with a black, fetid, empyreumatic, ponderous, and very thick Oil. Urge the fire to the utmost extremity, so that the retort may be of a perfect red heat. This violent fire will raise a little Volatile Alkali, besides a portion of Oil as thick as pitch. When the distillation is finished, you will find in the retort a black, saline, charred matter, which grows hot when wetted, attracts the

moisture of the air, runs *per deliquium*, and hath all the properties of a Fixed Alkali.

The mass, being exposed to a naked fire in the open air, burns, consumes, and is reduced to a white ash, which is a fiery, caustic, Fixed Alkali.

In accordance with the ruling concepts of his day, Macquer (erroneously) thought that the only result of dry distillation was the separation of the components of a mixture. He compared the results obtained from the pyrolysis of tartar, of the lees of wine and of the residue obtained by distillation of wine concluding (p 272) that

...liquors, which have undergone the spirituous fermentation, consist of an Ardent Spirit and a Tartarous Acid suspended in a certain quantity of water.

Pyrolysis was considered a valid method for the study of organic acids and of their derivatives, typically metallic salts. The prefix *pyro-* was assigned to the substances obtained by the action of heat without the addition of chemical reagents. *Pyro-acetic acid spirit* was obtained from acetates and in 1833 renamed as *acetone* (2) while the principal product obtained by the pyrolysis of tartaric acid was named *pyrotartaric acid*. A classification of organic acids into *volatiles* and *non-volatiles* was then proposed (19) on the basis of their behavior on being subjected to strong heat. It is interesting to note that such a distinction, although with a slightly different meaning, still has use in physiology, to indicate the kind of acids typically produced by the human body, and in botanical sciences. (Non-volatile acids are those that originate from the metabolic transformation of proteins contained in food, while the only volatile acid is carbonic acid.)

However, despite centuries of practice, dry distillation was still in its infancy (20):

The products resulting from the dry distillation of organic substances have recently been the subject of particularly thorough study. ... Despite the fairly important findings that have been made, it is evident that this subject is still in its cradle and that the so-called dry distillation of organic substances opens up an entirely new field in chemistry. ... The same substances—or mixtures of substances—may give rise to different products, according to temperature and the admixture of different inorganic substances.

By the involvement of skilled chemists, a rigorous chemical investigation of tartar could then start. Dedicated investigations of pyrotartaric acid were made by Théophile-Jules Pelouze (1807-1867), who believed that "the action of heat on tartaric acid represents one of the most interesting subjects from the history of pyrolyzed bodies" (21). According to Thomson (19, pp 63-64):

This acid [pyrotartaric acid] was made known to chemists in 1834. M. Pelouze obtained it by exposing tartaric acid to heat in a retort. (Ann. de Chim. et de Phys. lvi. 297)

When tartaric acid in a retort is kept at the temperature of 374° [Fahrenheit], a liquid passes into the receiver, which yields, when evaporated, pure crystals of *pyrotartaric acid*. But this process is so very tedious, that is better to distil at a temperature between 392° and 572°. The liquid that passes over is to be put into a retort and distilled to the consistence of a syrup. We must then change the receiver, and continue the distillation to dryness. The pyrotartaric acid is contained in this last liquid. When we surround it with a freezing mixture of snow and salt, or leave it to evaporate spontaneously, *in vacuo*, over sulphuric acid, yellow crystals are deposited. Dry these between folds of blotting paper, dissolve them in water, and agitate the boiling solution with animal charcoal, then crystallize. The crystals constitute pyrotartaric acid in a state of purity. (This acid may be obtained also by distilling cream of tartar in a retort. See the experiments of the Athenian, Alexandros Polaiologu Weniselos, in Ann. der Pharm. xv. 147.)

Pyrotartaric acid, thus obtained is in white crystals, which have an exceedingly sour taste, but no smell; and are very soluble in water and alcohol. When heated to 212° the acid melts, and it boils at 370°. This being very near the point of decomposition, it is difficult to volatilize it without residue. ... When racemic acid is distilled, it yields an acid identical with pyrotartaric acid.

Pelouze observed also that when tartaric or racemic acid is distilled in a retort, another acid besides pyrotartaric acid forms, which he considered to be acetic acid. (From the Latin *racemus*, "grape," racemic acid is a 1:1 mixture of D- and L-tartaric acid.) Justus von Liebig (1803-1873) first distinguished it from acetic acid and regarded it as a *liquid pyrotartaric acid* (22):

Liquid pyrotartaric acid. To prepare it, one subjects crystallized tartaric acid to a temperature of 200°C in a large tubulated retort with the aid of a spirit burner. The mass melts and soon swells considerably. ... Eventually, a heavy acidic liquid, with a strong smell of vinegar, distils and at the same time carbonic acid is liberated. When the distilled product begins being colored, the distillation is stopped. The residue in the retort is syrupy, dark-black colored, insoluble in water, soluble in water [*sic*; should be alcohol, as in the original German] and in alkali. ...

Solid pyrotartaric acid. This acid forms with low yield during the distillation of tartaric acid. It is obtained with higher yields by distilling the acidic potassium tartrate (Weniselos). To prepare it, a glass

retort is two-thirds filled with cream of tartar, which is then distilled; the colored acid obtained is subjected to evaporation in a water bath until crystallization starts; the solid pyrotartaric acid separates on cooling.

Jöns Jacob Berzelius (1779-1848) examined this liquid pyrotartaric acid in 1835 and eventually recognized it as a completely new substance (20):

... I pointed out that racemic acid on dry distillation produces an acid different from the pyrotartaric acid arising from tartaric acid, which has been well known for a long time. ... Although I have confirmed the findings of Pelouze that tartaric acid and racemic acid give the same distillation products, I did not reach the same conclusion that he did concerning the nature of the main part of the distillate, which he considered, because of its smell, to consist of acetic acid. This acid ... I called pyruvic acid and described as a volatile acid. I will go on using the name pyruvic acid, *acidum pyruvicum*, as an indication of its origin from the grape. The same acid is also found in the acidic fluid which is formed when solid potassium tartrate is submitted to dry distillation; it consequently occurs in an ancient remedy, *mixtura diatrion* or *m. pyrotartarica* [(23)] and deserves to be known for this reason as well.

The description made by Berzelius is a very accurate one (20):

I distilled a sample of tartaric acid in a tubulated glass retort on a sand bath, the temperature of which could be kept almost constant by increasing or reducing the draught. The mass started to give off a water clear distillate of a sharp taste, smelling of acetic acid, whereupon it melted, turned grayish, and began to foam.

When the material showed a tendency to boil over, the cork was removed from the tubular extension and a rigid platinum wire was introduced to break the foaming, which was easily accomplished. It was sometimes necessary to repeat this procedure. Without this precaution the distillation proceeds extremely slowly and the entire foaming mass collects in the upper part of the retort leaving the lower part empty. During the operation carbon dioxide is developed in a continuous stream, necessitating tubulation of the receiver, the end of the tube being submerged in water.

The content of the retort gets very sticky before the end of the operation, mostly due to condensed pyruvic acid. Later on in the operation the distillate gets more and more concentrated and becomes yellow in color, but even at the end is no more than pale yellow if the temperature does not exceed +220° (Celcius [*sic*]). The residue in the retort becomes more and more sticky, finally changing to a fluid which boils without foaming; the temperature is then about +200°, and

when the boiling is finished and nothing more distills at +200° the operation is finished. There is then left in the retort a mass which is soft while still hot but after cooling behaves like carbon.
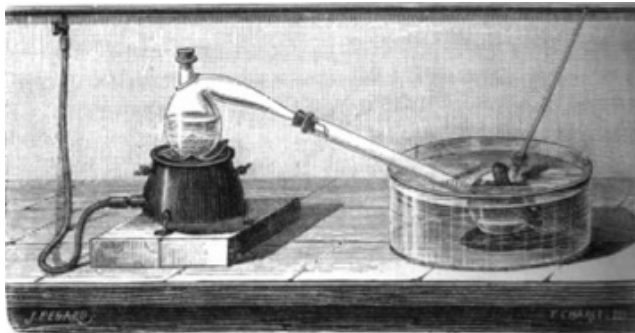

Figure 3. Eighteenth century distillation apparatus: retort and tubulated flask (24).

Berzelius was able to isolate pyruvic acid in a pure form by decomposing the lead salt with hydrogen sulfide. He was unable to obtain pure pyruvic acid by means of distillation alone because of its decomposition during heating (20).

Berzelius was a convinced promoter of the radical theory of organic compounds and he ended on considering pyruvic acid to be "a lower degree of oxidation of the same radical" as that of tartaric acid. In addition, on the basis of their formulae Berzelius found formic acid, tartaric acid, pyrogallic acid and pyruvic acid to be derived from the same organic radical.

Modern Organic Chemistry and the Solution of the Enigma

Several products can be obtained by heating tartaric acid at different temperatures. Two key processes are involved in their formation, namely dehydration (i.e.

loss of water) and decarboxylation (i.e. loss of carbon dioxide) (25). A prolonged heating at 150°C brings about the elimination of water from tartaric acid and the formation of tartaric anhydride, a white powder which readily recombines with water to give tartaric acid (26).

If the temperature is raised to 200°C decarboxylation of tartaric acid takes place and carbon dioxide is evolved while pyrotartaric acid is formed. At the same time, both tartaric acid and pyrotartaric acid decompose into pyruvic acid which in turn decomposes slightly into acetic acid by decarboxylation. Minor products are carbon monoxide, formic acid, acetoacetic acid and ethylene. It is evident that the nature and amount of these products is strongly dependent on the temperature at which pyrolysis is performed (27). Figure 4 summarizes the key steps of this process.

It is now possible to conclude that the product described by Nicholas Lémery as volatile salt of tartar, which appears as white clouds condensing in a solid when the tartar of wine is subjected to pyrolysis, is pyrotartaric acid also known as methylsuccinic acid. The formation of this product is typically followed by that of an *acid liquor* which is a mixture of pyruvic acid and acetic acid. The *tasteless phlegm* is the water produced by the dehydration of tartaric acid while the *huge amount of air* that impressed Macquer is carbon dioxide, generated by decarboxylation.
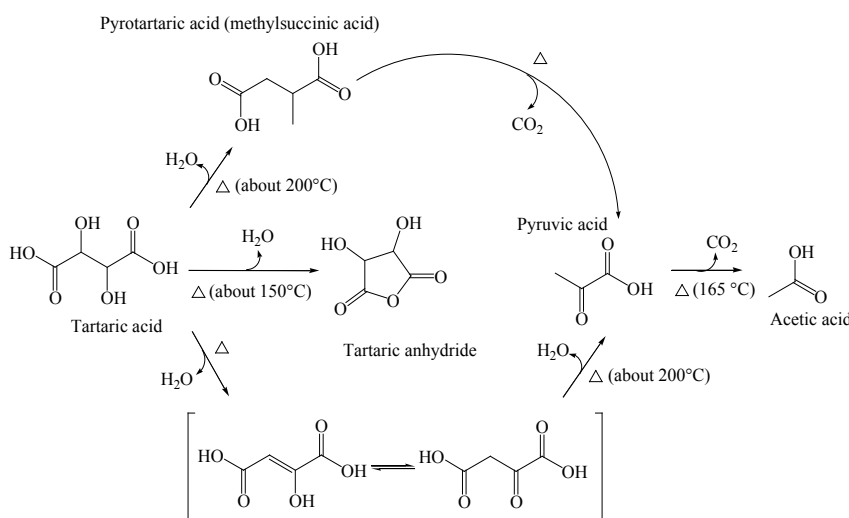
Figure 4. The principal processes involved in the pyrolysis of tartaric acid and the obtainable products.

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15. Reverberatory furnaces were used when high temperatures were required and were typically made of refractory bricks welded with a clay paste. The dimensions of these kilns varied depending on the size of the retorts to be employed. Retorts were supported by two iron bars placed inside directly on the fireplace, whose dimensions were such as to allow an easy ignition and maintenance of the fire. Under the fireplace were the air intake and the ashtray. The heat had to surround the retort completely to prevent the condensation of the vapors evolved from the processed substance, so the kiln was covered with a dome equipped with an exhaust vent for the fumes.

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About the Author

Guido Panzarasa, born in 1988, graduated from the Università del Piemonte Orientale "Amedeo Avogadro" in Materials Science (B.Sc., 2010) and in Chemical Sciences (M.Sc., 2012). He will obtain his PhD in Chemical Sciences at the same Institution in 2015, working in the field of polymer chemistry and nanotechnology, in particular polymer brushes. His research interests span from the development of innovative patterning strategies (*e.g.* photocatalytic lithography) to advanced characterization techniques (*e.g.* positron annihilation spectroscopy). His interest in the history of chemistry is focused on the analysis of ancient procedures and concepts with a contemporary chemistry approach.

HIST Award 2015

The recipient of the 2015 HIST Award of the Division of the History of Chemistry of the American Chemical Society is Professor Dr. Christoph Meinel of the University of Regensburg, Germany. This award is the successor to the Dexter Award (1956-2001) and the Sydney M. Edelstein Award (2002-2009), also administered by the Division of the History of Chemistry (HIST) of the American Chemical Society.

The HIST Award consists of an engraved plaque and a check. It was presented to Professor Meinel at the fall national meeting of the American Chemical Society in Boston in August 2015. Additional information about Prof. Meinel, the award, its past recipients, and its past incarnations can be found on the HIST website at http://www.scs.illinois.edu/~mainzv/HIST/awards/hist_award.php.

INTRODUCTION TO AN ENGLISH TRANSLATION, "ON THE DIFFERENT EXPLANATIONS OF CERTAIN CASES OF ISOMERISM" BY ALEKSANDR BUTLEROV

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This rather lengthy paper by Butlerov sought to bolster the case for the structural theory of organic chemistry by reconciling the apparently diametrically opposed views of Friedrich August Kekulé (1) and Hermann Kolbe (2). In retrospect, despite not being called a classic by the Alembic Club or Ostwald's Klassiker, this paper really does represent a watershed in the development of organic chemistry because a neutral third party with credibility in both camps served as the referee for the argument. Part of why it did not achieve "forgotten classic" status at the turn of the twentieth century is almost certainly the fact while that papers by the originators of structural theory, Kekulé and Couper, were recognized as classic contributions, Butlerov's enhancements of the theory, which were critical to its further development and acceptance, were viewed as being a lesser contribution. Butlerov's claims in this arena were also not helped by the blatant politicization of the history of science in the Soviet Union during the heyday of the cold war (3). However, today, as Butlerov's contributions are undergoing an impartial re-appraisal (4), it appears to me that this paper actually does deserve the title of "forgotten classic."

The decade between 1858 and 1868 was a tumultuous one for the discipline of organic chemistry. It saw the rise of the structural theory of organic chemistry from an esoteric theoretical construct to something that was so pervasive that by the end of the decade—still a year before Mendeleev first proposed his Periodic Law of the Elements—that few bothered to even acknowledge the work of the pioneers in the field (5). In its early years, it provoked a polemical debate over just what was meant by the structure of a compound, so it is perhaps the greatest testament to the success of the theory that, just a scant decade after it was first proposed, it was so widely accepted that it was viewed as a self-evident truth. There were four major participants in the polemical debates that gave rise to the structural theory of organic chemistry as it was used at the end of the decade—three protagonists and one antagonist.

A fierce struggle over priority ensued among the protagonists of the new theory (6). The first of these was Kekulé (1), whose deduction of the structure of benzene (7) assured him a place in the pantheon of great organic chemists. Contemporaneously with, and independent of Kekulé, the Scot, Archibald Scott Couper, working in the laboratory of Charles Adolphe Wurtz, developed his own structural theory of organic chemistry (8), but the delay in its publication led to him not receiving the credit he deserved. His intemperate—even vitriolic—allegations against Wurtz led to extremely bad blood between the two men, and to his summary dismissal from the laboratory. This was followed shortly thereafter by Couper suffering a nervous breakdown; he never again entered the debate. The third individual to enter this debate was Butlerov. Butlerov did not develop the basic concepts of structural theory, but his contribution was far more important. By making the theory easier to use, and by demonstrating its power by using it to predict the exis-

tence of compounds—whose existence he then confirmed by synthesis—he underscored just how powerful a tool this theory really was. In many ways, it was Butlerov who really made the new theory acceptable to the organic chemistry community; amongst other things, he wrote the first organic chemistry textbook (9) based solely on the new theory.

The main antagonist of the new theory was another giant of nineteenth-century organic chemistry, Hermann Kolbe. Kolbe was adamantly opposed to most new theories of organic chemistry, believing that *theories* had no place in an exact *experimental* science. Thus, structural theory, in its turn, also earned his unstinted opposition, as did its successor, the tetrahedral carbon of van't Hoff, and the subsequent rise of organic stereochemistry. It is rather a pity that this intemperate diatribe against the tetrahedral carbon atom (10) should be one of the most widely known of Kolbe's legacies, instead of, for example, his synthesis of acetic acid from undeniably inorganic precursors (11), or his electrolysis of carboxyl-ate salts to explore the structure of carboxylic acids (12).

Both Kekulé and Kolbe had their own version of structural theory, which Kolbe spoke of as the *rational constitution* of the molecule (he eschewed the term, "structure"). Nevertheless, a modern examination of both Kolbe's rational constitutions and Kekulé's structures for a number of compounds, in the light of modern atomic weights and the form of structural theory championed by Butlerov, reveals that they actually give the same struc-ture for the same compound. Indeed, one of Butlerov's early tasks was to show that the formulas of Kekulé and Kolbe, each of whom refused to acknowledge the possibility that the other might be correct, were actually the same. This reconciliation of the two views was not straightforward, since Kolbe used the earlier equivalent weights for carbon ($C = 6$) and oxygen ($O = 8$), which thus required the use of double atoms (C^2 and O^2) to get the correct weights of molecules, while Kekulé used the modern atomic weights for these elements, and used the barred symbols to specify this ($Ꞓ = 12$ and $Ꝋ = 16$). Butlerov first had to demonstrate that the two versions of the formulas of compounds were, in fact, equivalent. At the same time, he advanced a strong argument in favor of the new atomic weights. Kolbe eventually came around to this view, but he was still using the old equivalent weights when Butlerov's student, Markovnikov, was working in his laboratory as a post-doctoral researcher; one verbal battle over the atomic weight of oxygen was recounted by Markovnikov to his mentor (13). What is very interesting in Butlerov's paper is the fact that when one transforms

Kolbe's formulas by using the "new" atomic weights and the barred symbols, they are actually much easier to read and interpret than Kekulé's, and actually much closer to modern condensed structural formulas! Herein lay, in part, at least, the importance of Butlerov's version of structural theory: using it, he was able to reconcile the views of the two most influential chemists of his day—one a fierce protagonist of structural theory, and the other a fierce antagonist of the same theory. Being able to do this was critical to the universal acceptance of structural theory.

Following his reconciliation of the superficially di-vergent views of Kekulé and Kolbe, Butlerov—who first proposed the existence of double bonds in the alkenes, and triple bonds in the alkynes—then proceeds to explain in detail his version of structural theory. The treatment is highly logical, and he takes great pains to indicate where the point being made requires assumptions. He follows this by justifying those same assumptions with clear logic, and he thus slowly builds a coherent framework for use. With the exception of the formulas that he uses, his structures and his explanations of isomerism appear remarkably modern (although the emergence of stereo-chemistry would eliminate some of his errors—including an assertion that methyl chloride might possibly—he says, "probably"— exhibit isomerism).

Butlerov's French is relatively straightforward and easy to read, although he has a penchant for using semicolons to generate extremely long sentences to build logic strings. Many of his paragraphs consist of a single sentence made up of several clauses linked by semicolons. I have chosen to break up these sentences into segments that are more compatible with modern English prose. There are a number of terms that were current at the time that Butlerov was writing that are now relatively ambiguous or obscure. For this reason, I have translated "chemical force" by "chemical combining power," "atomicity" by "valence," "oxygenated carbon" by "carbonyl carbon," and "hydrogenated carbon" by "saturated alkyl carbon." Thus, a tetraatomic carbon atom becomes a tetravalent carbon atom. One word that has been especially problematic is "body." While a logical translation of this word in most places that it occurs is "substance," in other places, the word "molecule" is bet-ter; the word "species" is also used in places. The word "carbonyle" is also problematic, since Butlerov uses it two ways: to refer to what we call a carbonyl group today ($>C=O$), as well as to the methylene unit ($>C=$). Likewise, the verb "admettre" is translated variously as "acknowledge" or "accept." The word "exprimer" is

generally translated as "express," but in places, it is better translated as "describe."

A referee has raised the question of why Butlerov wrote this paper in French. This is an excellent question. Butlerov was fluent in both German and French, and had become acquainted with the new structural theory during his 1857-1858 *komandirovka* in western Europe. During that study abroad, he had spent six months in Paris, with Wurtz, and the remainder of the time in Germany, where he had met both Kekulé and Erlenmeyer. By his return to Russia, he had become an ardent proponent of structural theory, and immediately began teaching it as the basis for the study of organic chemistry (14).

At the same time, he clearly recognized Kolbe's pre-eminence and respected his abilities as a synthetic chemist; no fewer than three of his top students (K. M. Zaitsev, A. M. Zaitsev, and V. V. Markovnikov) studied with Kolbe. Although the younger Zaitsev (A. M.) was flexible (to the point of apostasy, in the eyes of Markovnikov, at least—he submitted an unsuccessful hand-written dissertation for the *kandidat* degree (15), describing Kolbe's views on rational constitution of organic and inorganic compounds)—Markovnikov resolutely defended his mentor's structuralist views in discussions with Kolbe (13).

The paper that is the subject of this translation culminates five years of work with structural theory on Butlerov's part. His first foray into the field was a comment (16) on Couper's paper of 1858, published in the *Annalen*. In the ensuing two years, Butlerov made a practice of publishing his synthetic work in French or German. It is interesting to note how the majority of papers that he published in French during this time also appeared in German. The converse was not true, which makes the referee's question particularly apropos. Unfortunately, I have no clear answer to it beyond mere speculation, which has no place in a scholarly journal.

I have followed the lead of Jensen and Kuhlman (17) in converting the footnotes in the original paper to sequentially numbered endnotes, placed after the body of the translation in conformity with the practice in the *Bulletin for the History of Chemistry*.

There is one place in the text (p 114 of the original) where Butlerov does appear to have mixed up the two compounds that he is discussing—ethylidene dichloride, CH_3CHCl_2, and ethylene dichloride, $ClCH_2CH_2Cl$. I have translated the text as originally written, but have made a translator's notation that this section appears to

be in error (otherwise his statements make absolutely no sense, and diverge from the careful argument that he has constructed). Likewise, there are places in the text where the structures given in the original are obviously wrong (fortunately, Butlerov provides examples immediately adjacent to the incorrect structures, so they are relatively obvious, and the correction required is also relatively obvious); in those cases, I have used the corrected structures in the body of the translation, and placed the original versions in the endnotes. All chemical structures have been re-drawn using modern drawing software to give a cleaner presentation in the translated paper than is available by simple scanning of the original document; the rigorous checking for accurate reproduction of the original was vital in identifying the errors alluded to above.

As with any translation, there are places where a literal rendering of the original language leads to stilted, or even ambiguous prose. In those cases, I have allowed myself a limited license to paraphrase the original French in order to convey the writer's meaning clearly and correctly to the English reader. These instances have been relatively rare, and have not, I believe, altered the meaning conveyed by the original work. This notwithstanding, any deficiencies in the current translation are the responsibility of the author.

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15.   (a) D. E. Lewis, "Aleksandr Mikhailovich Zaitsev: Markovnikov's Conservative Contemporary," *Bull. Hist. Chem.*, **1995**, *17/18*, 21-30. (b) D. E. Lewis, "A. M. Zaitsev: Lasting Contributions of a Synthetic Virtuoso a Century after his Death," *Angew. Chem. Int. Ed.*, **2011**, *50*, 6452-6458; "A. M. Saytzeff: bleibendes Vermächtnis eines Virtuosen der Synthesechemie." *Angew. Chem.*, **2011**, *123*, 6580-6586.

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PRIMARY DOCUMENTS
"ON THE DIFFERENT EXPLANATIONS OF CERTAIN CASES OF ISOMERISM"

Mr. A. Boutlerow
"Sur les explications différents de quelques cas d'isomerie,"
Bulletin de la Société Chimique de Paris, Nouvelle Série, **1864**, *1*, 100-128
Translated by David E. Lewis

Research in modern times has enriched the science by the discovery of some very instructive cases of isomerism, and shortly afterwards different attempts at a theoretical explanation of these facts appeared. The authors of some of these explanations, especially Messrs. Kolbe and Kekulé, appear, at first glance, to have chosen dissimilar starting points and have arrived at different conclusions. The explanations given by one, as by the other of these writers, merely consist of the difference in what one calls the chemical constitution of bodies. Although it is generally thought that the ideas of Mr. Kolbe and those of Mr. Kekulé on chemical constitution have no resemblance to each other, I believe that I can prove that their theoretical views are based on the same, or nearly the same fundamental principles, and that the difference in their conclusions is explained by the fact that these principles are not always applied in a manner that is sufficiently general and sufficiently rigorous. Now that we are beginning to move on from the school of Gerhardt, it is not difficult to note that the ideas formerly expressed by French chemists, and those of their opponents, were not always very far from each other. Sometimes, the difference lay in the form, rather than in the substance of these ideas.

Thus, on the basis of some theoretical views of Mr. Frankland, Mr. Kolbe is seen to express his thoughts on the saturation capacity of the elements (1) and at almost the sam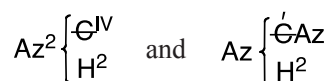e time, to pronounce himself vigorously opposed to the mechanical types of Mr. Dumas. Now, however, it is clear that these types only represent one way to express the saturation capacity of the elements, and that the new theoretical ideas of Mr. Kolbe, designed to explain the natural relationships between organic substances and mineral compounds, are themselves founded on the same principle—that of valence. By reading the classical treatise of Gerhardt and the treatise of Mr. Kolbe, one can well see that the two chemists attach a different significance to the word *constitution*, and that, at the same time, Gerhardt himself is almost forced to speculate on the chemical *constitution*, if one acknowledges this word in the sense that Mr. Kolbe gives to it. For Gerhardt, the molecular constitution is *the actual arrangement of the atoms* (2), and it is in the same sense that this term is accepted by Mr. Kekulé (3), while Mr. Kolbe speaks only of *points of attack* (Angriffs-Puncte) *of affinity*, and does not even believe that one day one might be able to judge the relative positions of the atoms in space (4). [The italics in this paragraph, and elsewhere in the translation, are in the original, unless otherwise noted. —DEL] At the same time, Gerhardt, seeking to interpret the action of chlorine on ethylene as a double decomposition *without the hydrogen chloride formed being released* (5), apparently acknowledges the possibility of judging the pre-existence of a fully-formed substance (hydrogen chloride) in the composition of the other, more complex, compound. The ideas of Mr. Kekulé on the possibility of determining the rational constitution of substances appear to be to be even

less removed from those of Mr. Kolbe, but the assertion of Mr. Kekulé that type formulas are only transformation formulas for substances (Umsetzungs-Formeln) (6) is likely, I believe, to throw this question into a certain obscurity. It is true that these formulas do not describe the constitution, if you wish to understand by this word the position of the atoms in space; but, at the same time, it is clear that Mr. Kekulé's formulas are intended, most often, to describe the chemical relationship of the elementary atoms that enter into the composition of the molecule (the points of attack of affinity, the constitution in the meaning given to this word by Mr. Kolbe). On the other hand, if one recalls the sense that Mr. Kolbe attaches to the word constitution, one cannot, for example, see in his hypothesis related to acetic compounds a way to describe the chemical bond that exists, 1) between the two carbon atoms, 2) between one of these atoms and an atom of oxygen, and 3) between the other carbon atom and three atoms of hydrogen. At the same time, it is evident that Mr. Kekulé, while speaking, for example, of the two molecules of water joined by the radical $\overline{SO}^2$ in a molecule of hydrated sulfuric acid, considers the two $H\Theta$ residues as the points of attack for the affinity of the sulfuryl radical. Further on, Mr. Kekulé explains himself on the same subject in a much clearer manner (7): *"These atoms," he says, "are linked to carbon in an indirect manner, through oxygen or nitrogen," or, "by the type of hydrogen, that is to say, one that is backed (anliegend) (8) by an atom of oxygen and not united with carbon except by means of this last atom."*
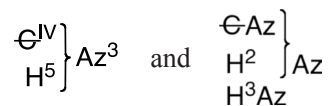
Messrs. Kolbe and Kekulé both want to determine the manner in which the elementary atoms are chemically linked to each other in a compound molecule. Mr. Kolbe designates this manner by the word *constitution*; for myself, I prefer the name *chemical structure*, a term to which no different meanings have yet been attached, and which, for that reason, is less likely to give rise to misunderstandings (9). I do not believe that it may be impossible, as Mr. Kekulé thinks (10), to specify on a map the position of the atoms in space: it is clear that mathematical formulas may well do it, and it is to be hoped that the laws that govern the formation of chemical molecules will one day find their expression with mathematics. I do not believe, either, with Mr. Kolbe, that once the existence of atoms is recognized, we would never get to determine their positions in space. I think it is useful for the moment to leave aside the atomic hypothesis that, although probable, is not yet necessary for our purely chemical considerations.

Whatever may be, it is clear that the theoretical considerations of Mr. Kekulé, as well as those of Mr. Kolbe, are based on the same principle, that of chemical structure. Since the important role of valence was recognized, this principle serves as the starting point for almost all theoretical views. It is found in the considerations of Mr. Wurtz on isomerization in hydrocarbons, in the radicals typical of Mr. Heintz and in the formulas of Mr. Wislicenus. It is two years since I tried to draw the attention of chemists to the necessity of substituting this principle for older theoretical ideas (see memoires on chemical structure, and on the affinities of polyvalent atoms, etc.). A sufficiently broad application of this principle, with all its consequences, will, I believe, be capable of settling all the disagreements that currently separate chemist theoreticians, while an application of the same principle with only little rigor will only serve to create new difficulties. That's how the difference in the formulas used by Messrs. Kolbe and Kekulé prevents their agreement, while, in going further, seeking the true meaning of these formulas, going back to the principle on which they are based, one recognizes that the difference is more apparent than real. One also sees that the rigorous application of the fundamental principle must lead to specific changes to erase the differences between the two chemists. After having accepted the principle of the chemical structure, one cannot say, as does Mr. Kekulé, that a substance can have several rational formulas, and one no longer has the need of types, which add nothing to the understanding of the formulas.

The facts lead to the admission that atoms act with a limited quantity of chemical combining power, and that each one of two atoms chemically linked one to the other uses, for this bond, at least one unit of its force. Thus, one unit of chemical combining power cannot act at the same time on two different atoms, and consequently it is clear that one formula describing the manner in which all the atoms of a molecule are chemically joined together must remain invariable, until it was acknowledged that the chemical bond of atoms is not what it describes. In every case, for one substance there is one and only one possible, truly rational formula. It is true that such a formula may have different forms; it could also be more or less complete as it describes the way in which all the atoms, or only some of them, are linked in the molecule, but it will always be the same formula, with more or less detail. Thus, one does not have the right to apply, at the same time, the two formulas

$$Az^2 \left\{ \begin{matrix} \overline{C}^{IV} \\ H^2 \end{matrix} \right. \quad \text{and} \quad Az \left\{ \begin{matrix} \overline{C}'Az \\ H^2 \end{matrix} \right.$$

to cyanamide, or the two formulas

$$\left. \begin{matrix} \overline{C}^{IV} \\ H^5 \end{matrix} \right\} Az^3 \quad \text{and} \quad \left. \begin{matrix} \overline{C}Az \\ H^2 \\ H^3Az \end{matrix} \right\} Az$$
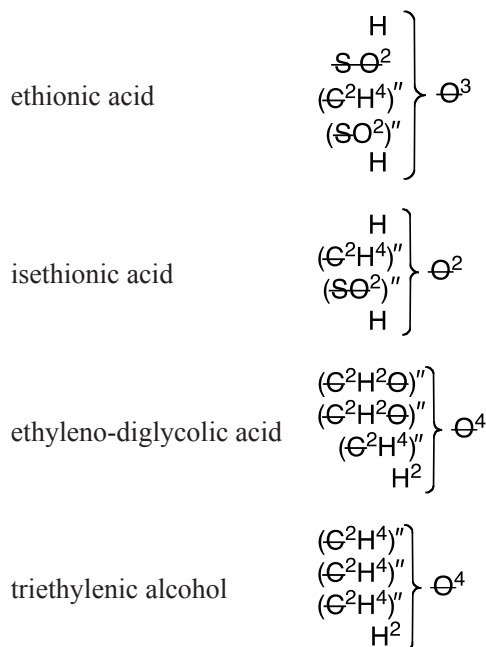
to guanidine (11). By following the principle that Mr. Kekulé himself accepts, we arrive at the conclusion that the first of these formulas does not have a well-defined meaning; it can be viewed as identical to the second formula, or it represents cyanamide as a combination of two divalent groups with the carbon atom, $\overline{C}$, that is to

say, as $\overline{C}^{IV}2(\overset{'''}{Az}H)''$; while the second formula positively expresses the idea that the substance in question contains an atom of cyanogen united with a monovalent residue of ammonia

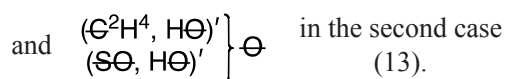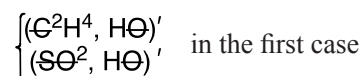$$\left. \begin{matrix} (\overline{C}^{IV}Az)' \\ H^2Az \end{matrix} \right\}$$
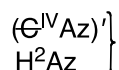
However, it is not immaterial whether one considers one atom of nitrogen joined to carbon by means of 3 units, and the other by only one unit of chemical combining power, or whether one thinks of each of the two nitrogen atoms joined to the carbon by two units of this force. From the first formula of guanidine, this base is formed by the union of $\overline{C}$ with $(AzH)''$ and $2(AzH^2)'$; from the second, it is the combination of $\overline{C}$ with Az''' and AzH^2 and with AzH^3, which is not at all the same thing. At the same time, the last formula of guanidine does not satisfy the demands of the principle of valence; the affinity of the carbon atom being saturated by Az''' and $(AzH^2)'$, this atom can no longer bind to ammonia. To represent the nitrogen of ammonia as acting, in this case, with all five units of its force, would be to allow the joining of the nitrogen atoms to each other. Among the formulas given by Mr. Kekulé, there are again, some that likewise contradict the principle of valence. The formula that he gives for acetal, for example, represents this substance (12) as resulting from the union of $\overline{C}^2H^4\Theta$ with two atoms of ethyl joined by Θ, that is to say, as a combination of two saturated molecules. From the formation of acetal, it appears much more likely that it is analogous to the diethyline of glycol [ethylene glycol diethyl ether —DEL], and that the difference between these two substances resides only in the difference between ethylene and ethylidene. The two substances would therefore be combinations of a divalent radical, $\overline{C}^2H^4$, with two

monovalent groups, $2(\overline{C}^2H^5,\Theta'')'$. Other formulas by Mr. Kekulé do not clarify the question of the manner in which the oxygen placed after the parenthesis serves to hold the different constituent parts in the molecule. These are the formulas of

ethionic acid
$$\left. \begin{matrix} H \\ S\Theta^2 \\ (\overline{C}^2H^4)'' \\ (S\Theta^2)'' \\ H \end{matrix} \right\} \Theta^3$$

isethionic acid
$$\left. \begin{matrix} H \\ (\overline{C}^2H^4)'' \\ (S\Theta^2)'' \\ H \end{matrix} \right\} \Theta^2$$

ethyleno-diglycolic acid
$$\left. \begin{matrix} (\overline{C}^2H^2\Theta)'' \\ (\overline{C}^2H^2\Theta)'' \\ (\overline{C}^2H^4)'' \\ H^2 \end{matrix} \right\} \Theta^4$$

triethylenic alcohol
$$\left. \begin{matrix} (\overline{C}^2H^4)'' \\ (\overline{C}^2H^4)'' \\ (\overline{C}^2H^4)'' \\ H^2 \end{matrix} \right\} \Theta^4$$

It appears possible to me to suppose that isethionic acid contains either the sulfuric acid radical, $(S\Theta^2)''$, or that of sulfurous acid, $(S\Theta)''$, as Mr. Carius thinks.

The formula showing the structure of this acid would be:

$$\left[\begin{matrix} (\overline{C}^2H^4, H\Theta)' \\ (S\Theta^2, H\Theta)' \end{matrix} \right. \quad \text{in the first case}$$

$$\text{and} \quad \left. \begin{matrix} (\overline{C}^2H^4, H\Theta)' \\ (S\Theta, H\Theta)' \end{matrix} \right\} \Theta \quad \begin{matrix} \text{in the second case} \\ (13). \end{matrix}$$

According to the first formula, the sulfur is directly linked to carbon, and according to the second, it is indirect, by means of the oxygen. In both these assumptions, one of the two residues, being joined to the hydrocarbon radical, must have the character of an alcohol; the other, linked to an oxygenated radical, must possess acidic properties, that is to say, those that characterize the same residue in acids. Based on the first assumption, which appears to be the more probable, isethionic acid would be closer to glycolic and lactic acids and their homologues. The difference between sulfurous and sulfuric acids would be due, based on the quantity of the chemical

combining power with which the sulfur acts. This element appears as tetravalent (S^{IV}) in the first, and as hexavalent (S^{VI}) in the second of these acids. The existence of the anhydrides SO^2 and SO^3 gives a certain degree of probability to the latter assumption.

Since the development of the ideas of valence, the meaning of Gerhardt's types has become obvious. It has been recognized that the service rendered to science by these types lies in the simple and clear way that they describe the degree of molecular complexity produced by atoms of different valence. It was also recognized early on that the four primitive types are no longer sufficient to show all the complexity due to pentavalent nitrogen and its analogues. In cases where the complexity depends on the polyvalency of carbon, an element that does not appear in the make-up of types, it was necessary to double or triple the Gerhardt types. Finally, in cases where three, four, or several polyvalent elements at a time are the reason for the binding of atoms in a molecule, the introduction of compound types was attempted. This, due as much to habit as to a real need, has not been able to clarify anything. The original simplicity of type formulas is no longer found in the compound types, and that is all the more so as, the complexities of the molecules produced by the influence of several polyvalent elements at a time being almost uncountable, it has become necessary to create a huge number of compound types. At the same time, these types no longer offer those advantages that made Gerhardt's types so useful to science. Considered by themselves, compound types do not describe the complications that are characteristic of their derivatives. Thus, the type (14)

$$\left.\begin{array}{c} H \\ [H] \\ H \\ H \\ H \\ H \\ H \\ H \end{array}\right\} \Theta \quad \Theta$$
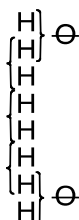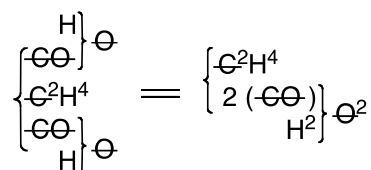
explains nothing by itself. It only has a meaning through the formulas of its derivatives, succinic acid and its homologues. As a molecule, this type is impossible: it does not satisfy the principle of valence. Compared to the formula of succinic acid, it only serves to point out the valence of the substituent residues, which can be done in an equally understandable and much more simple way by the accents (′) placed above or alongside formulas, and which are already in general use. Finally, the type formula given for succinic acid by Mr. Kekulé would make one believe that the HΘ residues are joined to this substance at the hydrocarbon group, while according to the theoretical ideas expressed by Mr. Kekulé himself, these residues are certainly combined with the carbonyl group, CO, and the two monovalent groups

$$\left.\begin{array}{c} CO \\ H \end{array}\right\} \Theta$$
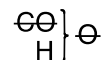
thus formed are linked to the divalent radical C^2H^4. This perspective, completely conforming to the views of Mr. Kekulé, can be expressed much more simply by a shorter formula, and without the need to derive any type; for example:

$$\left.\begin{array}{c} CO \\ C^2H^4 \\ CO \\ H \end{array}\right\} \Theta \quad = \quad \left\{\begin{array}{c} C^2H^4 \\ 2\,(CO) \\ H^2 \end{array}\right\} \Theta^2$$

In similar fashion, all other types are henceforth useless; the valences of atoms and residues, molecular complexities, and the analogues of substances can be designated without the use of types, which are only capable of describing that valence, those complexities, and those analogies.

Mr. Kolbe, like Mr. Kekulé and most other chemists, acknowledges that the elements are endowed with a limited quantity of chemical combining power, and that on the amount of valence of the elements depends the valence of compound residues. Thus, he views the "carbonyle" carbon, $C = C^2$, as the only cause of the trivalency of formyl C^2H, in which the fourth affinity of carbon is saturated by the atom of hydrogen (15). [This is not equivalent to a modern carbonyl carbon, >C=O, but, rather, to a modern methylene carbon, >C=. The author uses the same term with both meanings, so careful attention to context is required. —DEL.] These considerations of Kolbe, quite consistent with the prevalent theoretical views, necessarily imply the existence of saturated molecules, and lead to the examination of the manner in which the elementary atoms are linked in the molecule formed (chemical structure). These views are not modified one bit if one writes C^2 in place of C, and if one speaks of the carbonyl instead of an atom of carbon.

For Mr. Kolbe, as for everyone else, it is a fact that the minimum amount of carbon entering into chemical combinations is equal to 12, and that this minimum quantity is, furthermore, tetravalent. Like everyone else, he cannot yet explain why this quantity of carbon is neither less than 12, nor possesses another valence. But, by rigorously applying the principle that he acknowledges,

Mr. Kolbe must necessarily admit that when the chemical combining power of an atom or group is saturated, that atom or group becomes, as a result, incapable of chemical bonding. He must also admit that: the unit of chemical combining power residing in the methyl group belongs to the carbon atom; that trimethylamine contains three methyl radicals, because the nitrogen acts with three of its units of force; that, as a consequence, the nitrogen in this base is attached directly to the carbon, while the hydrogen, combined with the atoms of carbon, is only retained in the molecule by means of the latter element, and is in no way directly bonded to the nitrogen.

When considering ethylene, with Mr. Kolbe, as

$$\left.\begin{array}{c} C^2H^3 \\ H \end{array}\right\} C^2 \;=\; \left\{\begin{array}{l} \text{—}CH^3 \\ \text{—}CH \end{array}\right.$$
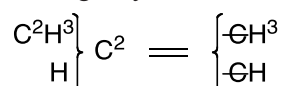
one evidently describes by this formula that the two carbon atoms are combined with each other by two units of affinity, that one atom of carbon is united to three, and the other to one atom of hydrogen, and that, as a consequence, the free affinities possessed by ethylene belong to one of the two carbon atoms encompassed by the molecule of ethylene.

We can ignore the question of the greater or lesser probability of this view. Still, however that may be, this is how one must interpret the formulas of Mr. Kolbe, if one wants to rigorously apply the fundamental principle acknowledged by him, and identical, as we have seen, to that which serves as the point of departure to the theoretical considerations of Mr. Kekulé and several other chemists.

Eventually it becomes necessary to examine not only the way in which the radicals, but also that in which the elementary atoms are combined into a compound molecule. At the same time, it must be allowed that each atom entering into the composition of the molecule is held there by the chemical combining power belonging to it and to another elementary atom.

These are, I believe, the necessary consequences of the principle [of valence —DEL]. However, Mr. Kolbe does not venture that far; he stops at examining radicals and how they combine, without entering into the details of the chemical structure of the radicals themselves. At the same time, he appears to allow the possibility of the combination of two saturated molecules (16). Analogous considerations, little compatible with the fundamental principle acknowledged by Mr. Kolbe are, in my opinion, the main reason for the disagreement that his theoretical views inspire with other chemists at the present time.

Thus, the formula HO (= 9) for water and the atomic weight O = 8 that Mr. Kolbe continues to use remove all resemblance to the type formulas of Mr. Kekulé.

Mr. Kolbe appears to agree, now, that the vapor density of substances is one *criterion* for determining their molecular weights, and we know that among the thousands of molecules measured, there is not a single authentic example of a substance containing one equivalent of oxygen (O = 8). But even if we do not pay attention to this circumstance, already very important, the ideas that Mr. Kolbe expresses on the ratio between carbon and other polyvalent elements are sufficient, by themselves, to lead to the adoption of the double atom of oxygen, $O^2 = \Theta$, and the formula $H^2\Theta$ for water.

For simple ethers and the anhydrides of monobasic acids, this scholar uses the generally acknowledged double formulas. Why and how are monobasic radicals bound in the molecule of the substance if the oxygen atom is not O = 16? And then, how will be explain the union of water with formula HO with the organic groups in the acid hydrates, etc.? In the molecule of acetic acid, $HO,C^2H^3(C^2O^2)O$, the valence of the tetravalent carbon (carbonyl = C^2) is completely saturated by the monovalent group C^2H^3 and by the 3 atoms of oxygen; on the other hand, the water, HO, is also a saturated molecule. So what, then, is the reason for the binding together of these two groups that do not possess the actual force to accomplish chemical combination? Likewise, the group

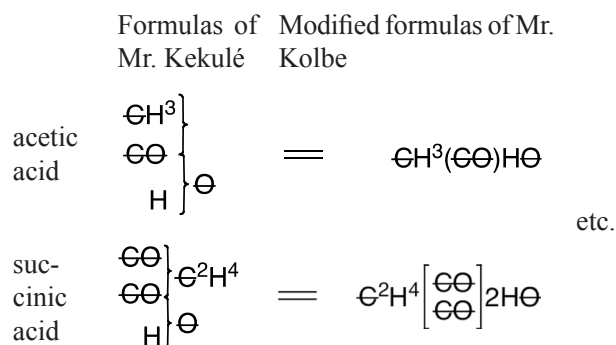$$C^2H^4\left[\begin{array}{c} C^2O^2 \\ C^2O^2 \end{array}\right]O^2$$
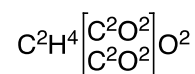
which Mr. Kolbe accepts in succinic acid combined with 2HO, being saturated, must be unfit to act chemically.

A large number of other formulas of this chemist give rise to similar observations. Is it not much more simple and more consistent to write $HO^2 = H\Theta$ instead of HO + O, and to consider this residue of a water molecule as monovalent and obeying the same principle with which Mr. Kolbe explains the trivalency of formyl C^2H, the monovalency of methyl, etc.? Is acknowledging the formula HO for water to deprive oneself, voluntarily, of the ability to trace the cause of the union of atoms in a group of complex compounds? I do not believe that using the old atom of oxygen and the formulas C^2O^2 and C^2O^4 for the oxide of carbon [carbon monoxide] and carbonic acid [carbon dioxide] are necessary to the views of Mr. Kolbe. It is true that many derivative organic substances cannot be obtained from these two compounds, as types, by way of substitution, but the theory loses nothing from that. Other types, like ΘH^4 or ΘCl^4 can render the same

service. For the theoretical views of Mr. Kolbe, like those of the majority of other chemists, it is essential that carbon be tetravalent, that it may also sometimes act with a part of its affinity, and that the atoms of this element have the capacity to bind to each other. The presence or absence of oxygen in compound types adds nothing to this perspective. In the formulas C^2O^2 and C^2O^4, the atoms of oxygen $O = 8$ are only representative of units of chemical combining power, and the symbols $Ɇ''$ and $Ɇ^{IV}$ are then both types of the oxide of carbon and carbonic acid. One may hope, I think, that the molecular formula for water, $H^2Ɵ = H^2O^2$ will soon be acknowledged by Mr. Kolbe, as he has already acknowledged the molecular formulas of ethers [esters —DEL] and anhydrides of the dibasic acids.

Now, if we introduce $HƟ$ for $HO + O$ into the formulas of Mr. Kolbe, and if we compare them to the formulas of Mr. Kekulé, remembering that both are designed, in principle, to describe the chemical structure of bodies, one must admit that in the majority of cases, these formulas are identical.

	Formulas of Mr. Kekulé	Modified formulas of Mr. Kolbe

acetic acid

$$\left. \begin{array}{c} ɆH^3 \\ ɆO \\ H \end{array} \right\} Ɵ \qquad = \qquad ɆH^3(ɆO)HƟ$$

etc.

succinic acid

$$\left. \begin{array}{c} ɆO \\ ɆO \\ H \end{array} \right\} Ɇ^2H^4 \left. \begin{array}{c} \\ \\ Ɵ \end{array} \right. \qquad = \qquad Ɇ^2H^4 \left[\begin{array}{c} ɆO \\ ɆO \end{array} \right] 2HƟ$$

To make the meaning of these formulas yet more obvious, it would, perhaps, be useful to modify them a little by acknowledging that the parenthesis on the left indicates a bond between the carbon atoms, and writing

acetic acid
$$\left\{ \begin{array}{c} ɆH^3 \\ ɆO \\ H \end{array} \right] Ɵ$$

succinic acid
$$\left\{ \begin{array}{c} \left. \begin{array}{c} H \\ ɆO \end{array} \right\} Ɵ \\ Ɇ^2H^4 \\ \left. \begin{array}{c} ɆO \\ H \end{array} \right\} Ɵ \end{array} \right.$$
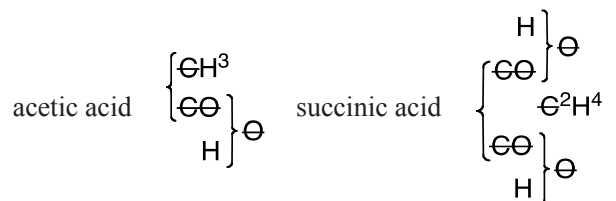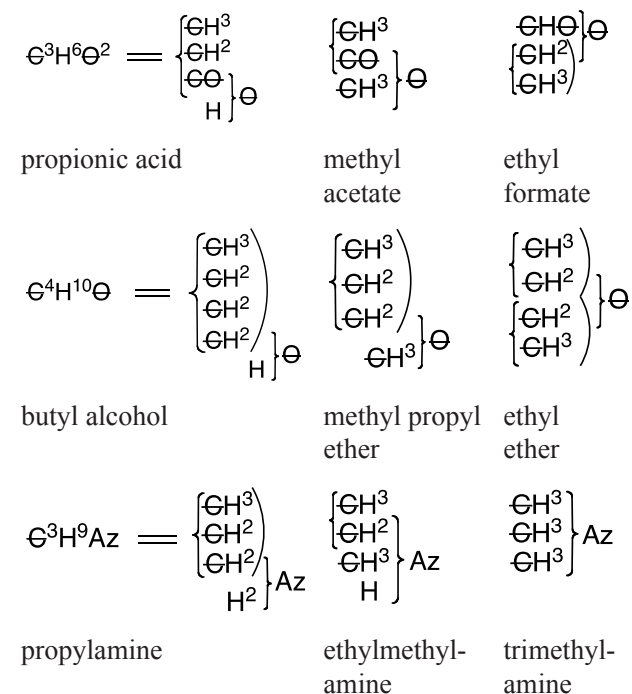
Finally, one must again note that the formulas of Mr. Kolbe often describe the details of the chemical structure better of molecules better than those of Mr. Kekulé. However, on breaking down these latter formulas, as Mr. Kekulé himself has done in certain cases, one generally arrives at *the same results*.

Passing onto the theoretical considerations by means of which Messrs. Kolbe and Kekulé seek to explain the isomerism of maleic and fumaric acids, etc., it will be noted first of all that the meaning of these views becomes especially clear when the principle of chemical structure, which serves as the starting point, is rigorously applied to the thoughts of these scholars as to their formulas.

To better understand the import of these thoughts, it is useful to realize the influence that the chemical structure of substances can generally exert on their isomerism.

The carbon atoms of an organic molecule are either joined directly through their affinity and a single polyvalent group that is bound further from other non-carbon atoms, or they form, by combining, several carbon-containing groups in which the carbon atoms, without being directly linked, are bound to the molecule through other polyvalent elements. In this way, we can produce a group of substances possessing the same molecular weight without being identical. This type of relationship between isomeric molecules is that which is ordinarily designated under the name of *metamerism*.

For example:

$$Ɇ^3H^6Ɵ^2 = \left\{ \begin{array}{c} ɆH^3 \\ ɆH^2 \\ ɆO \\ H \end{array} \right] Ɵ \qquad \left\{ \begin{array}{c} ɆH^3 \\ ɆO \\ ɆH^3 \end{array} \right\} Ɵ \qquad \left. \begin{array}{c} ɆHƟ \\ ɆH^2 \\ ɆH^3 \end{array} \right] Ɵ$$

propionic acid   methyl acetate   ethyl formate

$$Ɇ^4H^{10}Ɵ = \left\{ \begin{array}{c} ɆH^3 \\ ɆH^2 \\ ɆH^2 \\ ɆH^2 \\ H \end{array} \right] Ɵ \qquad \left\{ \begin{array}{c} ɆH^3 \\ ɆH^2 \\ ɆH^2 \\ ɆH^3 \end{array} \right] Ɵ \qquad \left\{ \begin{array}{c} ɆH^3 \\ ɆH^2 \\ ɆH^2 \\ ɆH^3 \end{array} \right\} Ɵ$$

butyl alcohol   methyl propyl ether   ethyl ether

$$Ɇ^3H^9Az = \left\{ \begin{array}{c} ɆH^3 \\ ɆH^2 \\ ɆH^2 \\ H^2 \end{array} \right\} Az \qquad \left\{ \begin{array}{c} ɆH^3 \\ ɆH^2 \\ ɆH^3 \\ H \end{array} \right\} Az \qquad \left. \begin{array}{c} ɆH^3 \\ ɆH^3 \\ ɆH^3 \end{array} \right\} Az$$

propylamine   ethylmethyl-amine   trimethyl-amine

But there is also another kind of isomerism, to speak less broadly: all the carbon atoms in the two isomeric molecules are linked directly to each other in both cases.

Thus, two carbon atoms form the group $\begin{cases} C \\ C \end{cases}$ in glycol as well as in glycolamide; this group is bonded, in both substances, to $(AzH^2)'$, to $(H\Theta)'$, to H^2, and to Θ, and yet these two substances are not identical.

This type of isomerism is explained by the mutual influence that atoms entering into the composition of a molecule exert on their reciprocal chemical character. Before specifying the details of this influence, it is essential to make an assumption, namely: each time that an atom acts with the same quantity of force in combining with other atoms, identical or not, it does not always act in the same way. This assumption does not, however, entirely abide by the facts: it is known that there are isomeric saturated hydrocarbons, C^nH^{2n+2}, and probably also isomers of methyl chloride, CH^3Cl. This has led me to acknowledge a difference in the units of force belonging to a carbon atom, that is to say, to acknowledge that two, or several atoms of carbon can combine with each other in different ways, and that a single atom of the same element can also combine in different ways with any other atom.

However, the influence of this difference is little known, and it appears probable that in every case it is less pronounced than the mutual influence of differing atoms entering into the composition of a molecule. The detailed study of the simplest organic compounds, those that contain only a single atom of carbon, promises to clarify the question of the differences in the units of chemical combining power belonging to that atom. However, until then it does not appear to be useful, in theoretical speculations, to take into consideration either this difference, or other, still problematic influences (the physical conditions under which the combination occurs, etc.). So, in choosing among the mutual chemical relationships of atoms where there is no doubt about the influence on their chemical character, and basing theoretical speculations only on these relationships, one can at least determine where the results of these speculations approach the truth, and what they still lack for that goal.

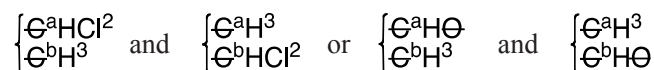Having acknowledged the assumption mentioned above, we arrive at the following conclusions:

Two atoms of carbon or any element, each taken separately, must be identical; they must necessarily still remain identical while they are combined with each other or both with the same elementary atoms. Each time that these atoms combine with the same quantity of their chemical combining power, the same group is formed.

Thus, the groups

$$\begin{cases} C^{VI} \\ C \end{cases} \qquad \begin{cases} C^{VIII} \\ C \\ C \end{cases} \qquad \text{etc.}$$
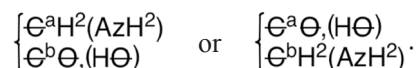
formed by the union of two or more carbon atoms must always have the same properties, and, as a consequence, the isomerism of two molecules formed by the union of such a group with other elements does not depend on the diversity of the groups formed by the carbon atoms. Two molecules having the same composition, and each containing, for example, the group $\begin{cases} C \\ C \end{cases}$ must remain identical if the role played by a carbon atom in the first case is filled by in the second by the other atom of this element. If we designate one of these carbon atoms by C^a and the other by C^b, and if these atoms are identical, then the two substances

$$\begin{cases} C^aHCl^2 \\ C^bH^3 \end{cases} \text{ and } \begin{cases} C^aH^3 \\ C^bHCl^2 \end{cases} \text{ or } \begin{cases} C^aH\Theta \\ C^bH^3 \end{cases} \text{ and } \begin{cases} C^aH^3 \\ C^bH\Theta \end{cases}$$

will also be identical. In the same way, it does not matter if glycine is

$$\begin{cases} C^aH^2(AzH^2) \\ C^b\Theta,(H\Theta) \end{cases} \text{ or } \begin{cases} C^a\Theta,(H\Theta) \\ C^bH^2(AzH^2) \end{cases}.$$

In general, *two molecules having the same empirical composition must be identical and not isomers if the chemical relationship between each elementary atom and all the other constituent parts of the molecule is the same in both cases, and, at the same time, two or more atoms of carbon or any other element entering into the composition of a molecule cannot be distinguished from each other by differences in the chemical relationship between each of these atoms and the other constituent parts of the molecule.*

Two or more atoms of an element occurring in the composition of a molecule can and must be different from each other when the chemical relationship between each of them and the other constituent parts of the molecule is not the same. It does matter, for example, if the chemical structure of the substance CH^4Cl^2 is that described by the formula $\begin{cases} CHCl^2 \\ CH^3 \end{cases}$ or that described by the formula $\begin{cases} CH^2Cl \\ CH^2Cl \end{cases}$. In the first case, the chemical relationship is the same between each atom of the same element and all
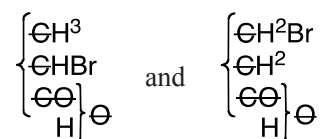
the other constituent parts; in the second case, it is the opposite. [It appears that Butlerov has reversed the two isomers here —DEL]

In glycine $\begin{cases} CH^2(AzH^2) \\ CO,(HO) \end{cases}$ and glycolamide $\begin{cases} CO,AzH \\ CH^2HO \end{cases}$, the chemical relationships of the constituent elementary atoms are no longer the same. The two atoms, identical in nature, on entering into the composition of the same molecule, take on a different chemical character when the influence exerted by each of them on the other constituent parts of the same molecule is different. The existence of this influence is a fact. It is easy to note that an element gives different relationships depending on the nature of the elements with which it is combined. Hydrogen atoms, for example, combined with carbon, behave with respect to other reagents in a manner other than those that are bound to oxygen, and this characteristic feature is conserved even within complex molecules. So it is that in alcohols, the hydrogen in the HO residue approximates the properties of the hydrogen of water, and the other hydrogen atoms, combined with carbon, generally give the same reactions as the hydrogen of hydrocarbons. Not only elementary atoms, but also compound groups influence the chemical character of atoms combined with them. The hydrogen of the residue HO, for example, while conserving the salient properties of hydrogen in water (oxidized hydrogen), behaves with reagents in different and characteristic ways depending on whether this residue is bound to a [modern—DEL] carbonyl carbon, in carboxylic acids, or a saturated alkyl carbon, in alcohols.
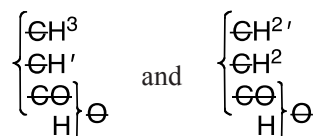
Thus, we see that the oxygen or hydrogen that is only bonded indirectly to the hydrogen of the HO residue, by means of carbon, nevertheless influences the character of the latter hydrogen. Based on such facts, we have the right to say, in general, as I have already noted in one of my previous papers, that elementary atoms in the interior of a molecule can exert a reciprocal influence on their chemical character without having to be directly linked. This explains the differences in the properties of glycine and glycolamide. In the first, the HO residue is combines with a carbonyl carbon as in an acid, and the AzH^2 residue is linked to a saturated alkyl carbon as in the amines. In the molecule of the second substance, the opposite takes place: the HO residue is bound to a hydrocarbon group, as in the alcohols, and the AzH^2 residue is combined with a carbonyl carbon as in the acid amides.

Of course, such facts naturally lead to the conclusion that the constituent atoms of a molecule can exert a reciprocal influence, though perhaps less pronounced,

when they are bonded in an even more indirect way. Thus, one will obtain, for example, two isomeric, non-identical substances from propionic acid by replacing one hydrogen of the saturated alkyl carbon combined with the group $\begin{cases} CO \\ H \end{cases} O$, by bromine, and then one hydrogen of the other saturated alkyl carbon:

$$\begin{cases} CH^3 \\ CHBr \\ CO \\ \quad H \end{cases} O \quad \text{and} \quad \begin{cases} CH^2Br \\ CH^2 \\ CO \\ \quad H \end{cases} O \ .$$

Speaking of the propionic acid residue $C^3H^6O^2 - H = (C^3H^5O^2)'$, we also have the right to say that there may be two isomeric residues,

$$\begin{cases} CH^3 \\ CH' \\ CO \\ \quad H \end{cases} O \quad \text{and} \quad \begin{cases} CH^{2'} \\ CH^2 \\ CO \\ \quad H \end{cases} O \ .$$

One must remember, on the other hand, that the chemical character of an atom depends very much more on the nature, rather than the number of atoms with which it is combined. In effect, the properties of the HO residue are closely allied in propyl alcohol and allyl alcohol, even though the quantity of hydrogen in the hydrocarbon radical to which this residue is combined is not the same in the two substances.

By following this line, one will come to the conclusion that six isomeric dibromobutyric acids can exist. By designating as A the group $\begin{cases} CO \\ H \end{cases} O$, these acids will be represented by the following formulas:

$$C^4H^6Br^2O^2 = C^3H^5Br^2A =$$

I.   II.   III.   IV.

$$\begin{cases} CHBr^2 \\ CH^2 \\ CH^2A \end{cases} \begin{cases} CH^3 \\ CBr^2 \\ CH^2A \end{cases} \begin{cases} CH^3 \\ CH^2 \\ CBr^2A \end{cases} \begin{cases} CH^2Br \\ CHBr \\ CH^2A \end{cases}$$

V.   VI.

$$\begin{cases} CH^3 \\ CHBr \\ CHBrA \end{cases} \begin{cases} CH^2Br \\ CH^2 \\ CHBrA \end{cases}$$
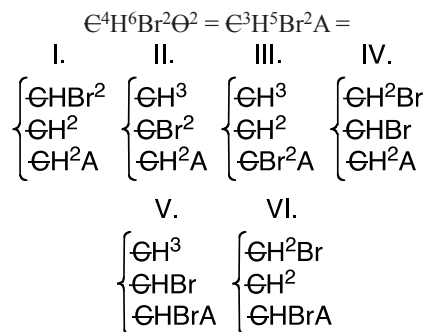
The relationship between the two bromine atoms and the other constituent parts is, as can be seen, different in each one of these formulas, but it is noteworthy that the difference is not of the same kind in the six cases. In formulas I and IV all the bromine is bonded to the

saturated alkyl carbon not combined with the group A; in two other cases, described by formulas V and VI, one brominated carbon atom is bound to a saturated alkyl carbon, and the other brominated carbon atom is bound to the carbonyl carbon (of the group A). The bromine occurs therefore under almost the same influence in cases I and IV as in cases V and VI. As it is not likely that the amount of hydrogen combined to the brominated carbon exerts a marked influence on the chemical character of the bromine atoms, we have the right to expect that bodies I and IV, on the one hand, and bodies V and VI on the other, will be almost identical, and that the number of verifiable isomers of dibromobutyric acids will thus be reduced to four instead of six. I will not insist on the accuracy of these conclusions, but I would suggest that these theoretical considerations are a logical consequence of the principle of chemical constitution, and that, at the same time, the need for the application of this principle, itself generally follows from generally acknowledged ideas about valence and the chemical molecule.

Mr. Kekulé has expressed his considerations of isomerism only briefly; this is why it is difficult to make a positive decision about the meaning of his views. It must be noted, however, from the beginning, that when he speaks of the position of atoms using this term, this chemist means only their chemical bonding in the molecule (the *chemical* structure, or constitution in the sense of the word acknowledged by Mr. Kolbe) [italics mine —DEL]. In effect, it is this bonding and not the position of the atoms in space that is essential to the considerations of Mr. Kekulé. In fact, every speculation with respect to this latter aspect based on chemical reactions would be in direct contradiction with what Mr. Kekulé expresses in his course of organic chemistry (17).

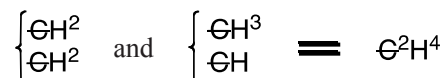Concerning the structure of succinic acid and its congeners, Mr. Kekulé will undoubtedly acknowledge, as does Mr. Kolbe, that the two $\left.\begin{array}{c} CO \\ H \end{array}\right\}O$ groups that occur in all these substances and are always identical to each other, cannot have any significance for the isomerism. One would be perfectly right, therefore, to acknowledge, with Mr. Kolbe, that the cause of the isomerism of maleic and fumaric acids or of the dibromosuccinic acids must be sought in the isomerism of the $Є^2H^2$ and $Є^2H^2Br^2$ groups. But on the other hand, the chemical structure of ethylene, from which these two groups are derived, is not the same according to these two scholars. Mr. Kekulé believes that it is symmetric $\left\{\begin{array}{c} Є H'^2 \\ Є H^{2\prime} \end{array}\right.$, and that consequently, the 2 free

units of chemical combining power in the substance in question belong to two different carbon atoms, while Mr. Kolbe acknowledges for ethylene the formula

$$\left.\begin{array}{c} ЄH^3 \\ H \end{array}\right\} Є \quad = \quad \left\{\begin{array}{c} ЄH^3 \\ ЄH'' \end{array}\right.$$
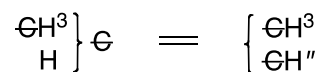
which says the affinity of one of the carbon atoms is completely saturated, and that the two atoms of this element consequently occur in a different chemical state. In effect, the existence of two isomeric bodies

$$\left\{\begin{array}{c} ЄH^2 \\ ЄH^2 \end{array}\right. \quad \text{and} \quad \left\{\begin{array}{c} ЄH^3 \\ ЄH \end{array}\right. \quad = \quad Є^2H^4$$
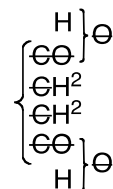
appears to be possible, but there is reason to think that the actual chemical structure of ethylene is described by the first formula, rather than the second. It is known that acetaldehyde contains, in all probability, a methyl group, $ЄH^3$, and that the group $Є^2H^4$ (ethylidene of acetaldehyde, which is isomeric and non-identical with olefiant gas) possesses the chemical structure described by the formula $\left\{\begin{array}{c} ЄH^3 \\ ЄH \end{array}\right.$ (18). At the same time, ethylene is formed, as I have shown, when a $ЄH^2$ group (methylene)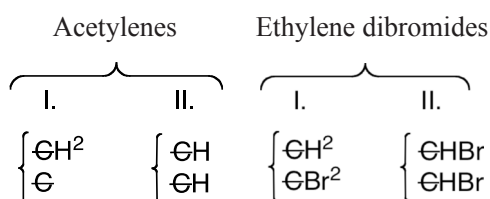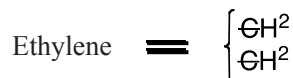 is released. By accepting the formula $\left\{\begin{array}{c} ЄH^3 \\ ЄH \end{array}\right.$ for ethylene, one must also accept that for it to be formed, one of the two $ЄH^2$ groups loses an atom of hydrogen, and the other gains one, under the same conditions. This is not likely.

Whatever it may be, it is certain that it is actually ethylene that is involved in the composition of succinic acid, and accepting the ideas of Mr. Kekulé with respect to the chemical structure of ethylene, the rational formula of this acid will be

$$\left\{\begin{array}{c} \left.\begin{array}{c} H \\ ЄO \end{array}\right\}O \\ ЄH^2 \\ ЄH^2 \\ \left.\begin{array}{c} ЄO \\ H \end{array}\right\}O \end{array}\right.$$

The two saturated alkyl carbon atoms are thus in the same state, therefore it is not clear why the derivatives produced by the elimination of two atoms of hydrogen belonging, on the one hand, to one, and, on the other hand, to the other carbon atom must be isomers and non-identical, as Mr. Kekulé assumes. On the other hand, from the way that that chemist views it, a third isomeric acid must exist: this is the one formed by loss of half the hydrogen from each one of the two saturated alkyl

carbons. Along with Mr. Kolbe, we allow that while keeping the formula $\left\{\begin{array}{l} CH^2 \\ CH^2 \end{array}\right.$ for ethylene, the hydrogen lost or substituted in the formation of maleic and fumaric acids, or in the dibromosuccinic acids comes on the one hand from two, and on the other hand, from a single carbon atom. Thus, we have two acetylenes and two genuine isomeric dibromoethylenes.

$$\text{Ethylene} \;=\; \left\{\begin{array}{l} CH^2 \\ CH^2 \end{array}\right.$$

Acetylenes   Ethylene dibromides

I.	II.	I.	II.
$\left\{\begin{array}{l} CH^2 \\ C \end{array}\right.$	$\left\{\begin{array}{l} CH \\ CH \end{array}\right.$	$\left\{\begin{array}{l} CH^2 \\ CBr^2 \end{array}\right.$	$\left\{\begin{array}{l} CHBr \\ CHBr \end{array}\right.$

For the formula $\left\{\begin{array}{l} CH^3 \\ CH \end{array}\right.$ for ethylene, one obtains, as Mr. Kolbe acknowledges, two isomeric acetylenes identical to those whose formulas have just been given, and two dibrominated ethylenes (19).

$$\left\{\begin{array}{l} CH^2Br \\ CBr \end{array}\right. \qquad \left\{\begin{array}{l} CHBr^2 \\ CH \end{array}\right.$$
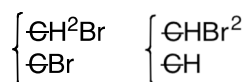
So we see, in brief, that with the one formula for ethylene, as with the other, one comes to analogous results (20). The formula of Mr. Kekulé is more probable, but when one rigorously applies the fundamental principle, the conclusions that Mr. Kolbe comes to appear to be more reasonable (21).

The case of isomerism in the dibrominated pyrotartaric acids and the three aconic acids (mesaconic acid, citraconic acid, and itaconic acid) is not quite analogous to the previous one. In two cases, one is obliged to seek the cause of the isomerism of the acids in the isomerism of the allylene or propylene dibromides. However, if one accepts the chemical structure for propylene described by the formula
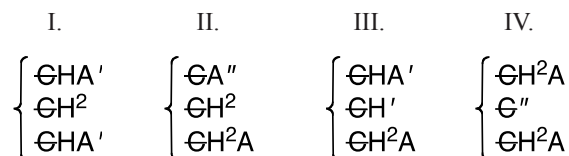
$$\left\{\begin{array}{l} CH'^2 \\ CH^2 \\ CH'^2 \end{array}\right.$$
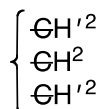
the atoms of this hydrocarbon are not all under the same chemical conditions as are the carbon atoms of ethylene

$$\left\{\begin{array}{l} CH'^2 \\ CH'^2 \end{array}\right.$$. By again designating the group $\begin{array}{c} CO \\ H \end{array}\Big\rangle O$ by A, the chemical structure of pyrotartaric acid is described by the formula

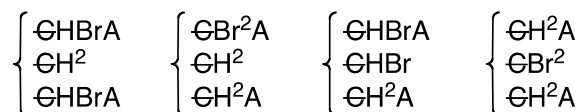$$\left\{\begin{array}{l} CH^2A \\ CH^2 \\ CH^2A \end{array}\right.$$
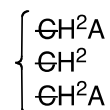
that is to say, in this case two carbon atoms are combined not only with saturated alkyl carbon and hydrogen, but also with a carbonyl carbon, while the third atom of this element is bonded only to alkyl carbon and hydrogen. It thus appears probable that the two substances produced by substitution or elimination of hydrogen belonging to either of the first two carbon atoms are identical to each other, but different from that which is formed when the third group, CH^2, undergoes the same transformation. The point of view of Mr. Kekulé, who thinks that two hydrogen atoms bonded to the same carbon atom are always eliminated or substituted, thus leads us to assume that there are only two cases of isomerism that can exist. But no more than in the case of the derivatives of succinic acid does it explain why the elimination or substitution of hydrogen atoms bonded to different carbon atoms is impossible. On the contrary, acknowledging that the hydrogen eliminated or substituted may equally well come from one carbon atom alone, or two atoms of pyrotartaric acid, one obtains the four following isomers:
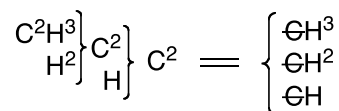
Unsaturated acids.

I.	II.	III.	IV.
$\left\{\begin{array}{l} CHA' \\ CH^2 \\ CHA' \end{array}\right.$	$\left\{\begin{array}{l} CA'' \\ CH^2 \\ CH^2A \end{array}\right.$	$\left\{\begin{array}{l} CHA' \\ CH' \\ CH^2A \end{array}\right.$	$\left\{\begin{array}{l} CH^2A \\ C'' \\ CH^2A \end{array}\right.$

Dibrominated acids.

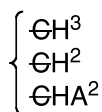|			
$\left\{\begin{array}{l} CHBrA \\ CH^2 \\ CHBrA \end{array}\right.$	$\left\{\begin{array}{l} CBr^2A \\ CH^2 \\ CH^2A \end{array}\right.$	$\left\{\begin{array}{l} CHBrA \\ CHBr \\ CH^2A \end{array}\right.$	$\left\{\begin{array}{l} CH^2A \\ CBr^2 \\ CH^2A \end{array}\right.$

In the same way, one can form conclusions about the possible isomers for malic and tartaric acids.

If, along with Mr. Kolbe, we describe the chemical structure of propylene by the formula (22)
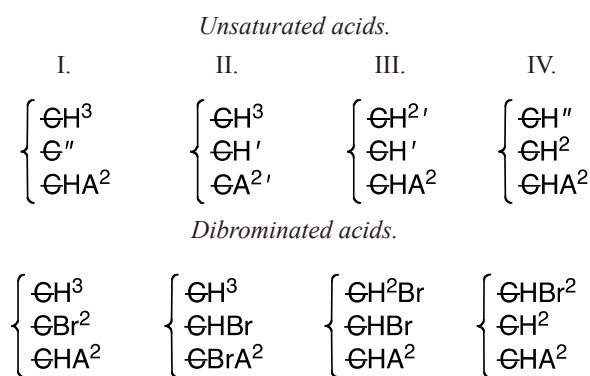
$$\left.\begin{array}{c} C^2H^3 \\ H^2 \end{array}\right\}C^2\Big\} \begin{array}{c} \\ H \end{array}\Big\} C^2 \;=\; \left\{\begin{array}{l} CH^3 \\ CH^2 \\ CH \end{array}\right.$$

pyrotartaric acid will be described by the formula

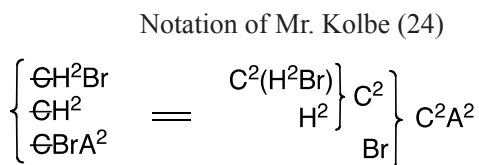$$\left\{\begin{array}{l} CH^3 \\ CH^2 \\ CHA^2 \end{array}\right.$$

The three carbon atoms in this substance thus occur in different chemical states, but the differences are not the same for each of them. One of the three carbon atoms is bonded to a carbonyl carbon, a saturated alkyl carbon, and to hydrogen; the two others are bonded only to saturated alkyl carbon and hydrogen, but to a different amount of the latter element. One may assume from that, that the latter differences, as noted above, will be less pronounced, and possibly even almost nothing. Whether the differences in the three carbon atoms are acknowledged or not, the conclusions arrived at by Mr. Kolbe appear to be doubtful.

By translating the formulas of Mr. Kolbe, as we have done above, one obtains (23)

Unsaturated acids.

I.   II.   III.   IV.

$$\left\{\begin{array}{l} CH^3 \\ C'' \\ CHA^2 \end{array}\right. \quad \left\{\begin{array}{l} CH^3 \\ CH' \\ CA^{2'} \end{array}\right. \quad \left\{\begin{array}{l} CH^{2'} \\ CH' \\ CHA^2 \end{array}\right. \quad \left\{\begin{array}{l} CH'' \\ CH^2 \\ CHA^2 \end{array}\right.$$

Dibrominated acids.

$$\left\{\begin{array}{l} CH^3 \\ CBr^2 \\ CHA^2 \end{array}\right. \quad \left\{\begin{array}{l} CH^3 \\ CHBr \\ CBrA^2 \end{array}\right. \quad \left\{\begin{array}{l} CH^2Br \\ CHBr \\ CHA^2 \end{array}\right. \quad \left\{\begin{array}{l} CHBr^2 \\ CH^2 \\ CHA^2 \end{array}\right.$$
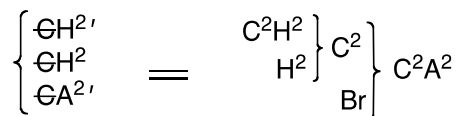
It is apparent therefore that the substances whose chemical structures are described by formulas III and IV are almost identical if the character of the two carbon atoms, which only differ in the *quantity* of hydrogen to which they are bound, is the same. In effect, the bromine or the free affinity belonging to saturated alkyl carbon atoms not bounded to group A in bodies (III) and (IV) only differ in the degree of hydrogenation.
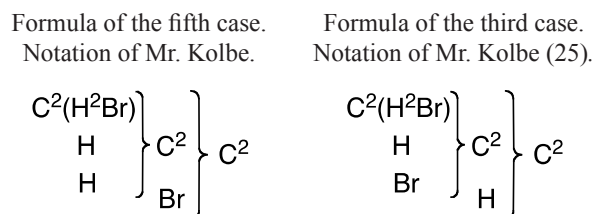
Should one want to acknowledge preferably that the three atoms of propylene are different, one must conceive of the possibility of the existence of not four, as Mr. Kolbe assumes, but five isomeric acids. In fact, besides the four cases pointed out by this chemist, the following case must also have a place:
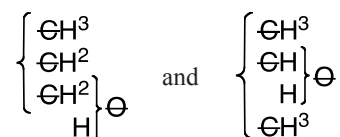
Notation of Mr. Kolbe (24)

$$\left\{\begin{array}{l} CH^2Br \\ CH^2 \\ CBrA^2 \end{array}\right. \quad = \quad \left.\begin{array}{c} C^2(H^2Br) \\ H^2 \\ Br \end{array}\right\}C^2 \quad \right\}C^2A^2$$

Notation of Mr. Kolbe

$$\left\{\begin{array}{l} CH^{2'} \\ CH^2 \\ CA^{2'} \end{array}\right. \quad = \quad \left.\begin{array}{c} C^2H^2 \\ H^2 \\ Br \end{array}\right\}C^2 \quad \right\}C^2A^2$$
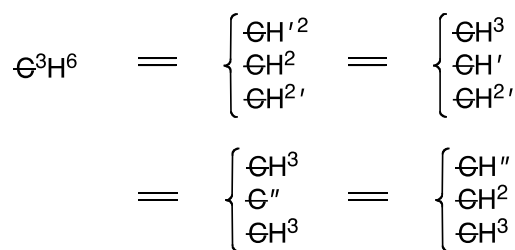
The bodies described by these formulas are no less different from the preceding ones than those are from each other. In addition, there is no reason why this fifth case should be contradictory to Mr. Kolbe's views because the only difference between the formulas that describe it [the fifth isomer —DEL] and some of this scholar's other formulas being the place that is occupied by an atom of bromine or a free affinity. For example:

Formula of the fifth case.   Formula of the third case.
Notation of Mr. Kolbe.   Notation of Mr. Kolbe (25).

$$\left.\begin{array}{c} C^2(H^2Br) \\ H \\ H \\ Br \end{array}\right\}C^2 \quad \right\}C^2 \qquad \left.\begin{array}{c} C^2(H^2Br) \\ H \\ Br \\ H \end{array}\right\}C^2 \quad \right\}C^2$$

Mr. Kolbe tries to explain the isomerism of propyl alcohols by deriving their formulas by substitution. It should be noted here, as everywhere else, that the rigorous application of the principle of chemical structure appears to provide a better method to estimate the true scope of these speculations. This principle, like the preceding substitution used by Mr. Kolbe, permits the prediction of two isomeric alcohols.

$$\left.\begin{array}{l} CH^3 \\ CH^2 \\ CH^2 \\ H \end{array}\right\}O \quad \text{and} \quad \left.\begin{array}{l} CH^3 \\ CH \\ H \\ CH^3 \end{array}\right\}O$$

The first of these formulas is the one that Mr. Kolbe gives to normal propyl alcohol; the second corresponds to the alcohol obtained by hydrogenation of acetone. The same principle leads to the assumption that four isomeric propylenes exist:

$$C^3H^6 \quad = \quad \left\{\begin{array}{l} CH'^2 \\ CH^2 \\ CH^{2'} \end{array}\right. \quad = \quad \left\{\begin{array}{l} CH^3 \\ CH' \\ CH^{2'} \end{array}\right.$$

$$= \quad \left\{\begin{array}{l} CH^3 \\ C'' \\ CH^3 \end{array}\right. \quad = \quad \left\{\begin{array}{l} CH'' \\ CH^2 \\ CH^3 \end{array}\right.$$

The first two, whose carbon atoms differ only in the amount of hydrogen to which they are bonded, are probably closer to each other than to the third, which contains a carbon atom without any hydrogen, and the fourth will perhaps be almost identical to the second.

One runs the risk of coming to unlikely conclusions, if, losing sight of the chemical structure of the bodies that react and that of the bodies produced, one speculates on the relationships that exist between their composition and the composition of other substances. As an instructive example, we may cite the considerations of Mr. Kolbe on the di- and tri-glycolamidic acids (26) obtained by Mr. Heintz. Regarding the formation of glycine and these interesting bodies, there is nothing simpler than the following: their formation is perfectly analogous to the formation of methylamine, and di- and tri-methylamine, when these bases are obtained by the action of methyl bromide on ammonia. In all these cases, the reaction consists of a simple double decomposition where the monovalent residue, formed by loss of a halogen atom from the organic molecule, binds with the ammonia residue. Since the nitrogen of the ammonia acts with three units of chemical combining power, it is possible to form three species in which one atom of the residue and two atoms of hydrogen, or two atoms of the residue and one atom of hydrogen, or eventually three atoms of the residue, are bound in one molecule by the affinity of nitrogen. In the case of the formation of Mr. Heintz's acids, the organic residue is:

$$(C^2H^3O^2)' \ == \ C^2H^3ClO^2 \ - \ Cl \ == \ \left\{ \begin{array}{l} (CH^2)' \\ CO \\ H \end{array} \right\} O \, .$$
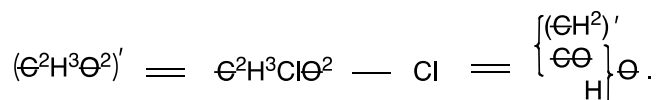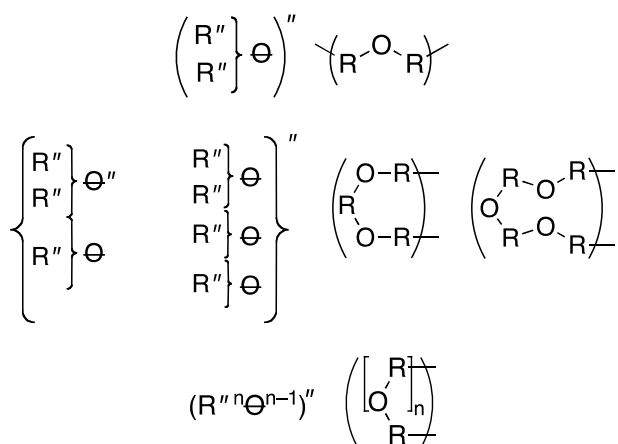
After that, it is entirely superfluous to accept the production of an unsaturated molecule (monochloroacetic acid *less* hydrogen chloride), as does Mr. Kolbe, and we easily envisage that with concentrated ammonia, the primary product is formed, and with dilute ammonia the secondary and tertiary products are formed predominantly. It becomes evident, at the same time, that diglycolamidic acid corresponds to aspartic acid as does dimethylamine to ethylamine, which is to say that here exists a genuine *metamerism*. In the molecule of aspartic acid, as in those of succinic, malic and other acids, and in ethylamine, all the carbon atoms are directly bonded to each other. In the molecule of the di- and triglycolamidic acids, as in that of di- and trimethylamine, they are only bonded through the nitrogen atom acting through its three units of chemical combining power.

The facts demonstrate that, in general, atoms or groups bonded indirectly in a molecule through other intermediate atoms, split apart when the latter atoms are lost. This is the way, for example, that alcohol radicals, held together in ethers by the divalent oxygen atom, split apart by the action of phosphorus iodide, and one obtains two molecules of the organic iodide from one molecule of ether because the divalent oxygen is replaced by iodine, whose atoms, because of their monovalency, cannot serve to join two or more other atoms. Following these guidelines, we can positively assume that the polyglycolamidic acids of Mr. Heintz will split into molecules containing only C^2 (probably glycolic acid), once their nitrogen is removed by the action of hyponitric acid.

It is more likely, Mr. Wurtz assumes, that diglycolic acid will result from the action of nitrous acid on diglycolamidic acid. In that case, the units of chemical combining power belonging to the organic residues will be saturated at the moment of reaction, not separately by HO residues, as it should be during the formation of glycolic acid, but both together by an oxygen atom. However, to accept such a metamorphosis (in the presence of water), it would be necessary to observe an analogous reaction for triglycolamidic acid, and to me, this seems to present some difficulties. In fact, I think that there must exist a diglycolamidic acid metameric with that of Mr. Heintz, and that will be to diglycolic acid as glycine is to diglycolic acid, and that will give the latter by the action of nitrous acid. These ideas, which lead me to this assumption, and that are derived from the principle of chemical structure, may be able to clarify, to a certain point, some questions concerning the nature of polyacids, polyalcohols, and their congeners. It is known that the elegant research of Mr. Wurtz has shown that ethylene oxide, on reacting with ammonia, gives rise to a series of oxygenated bases, some of which contain in their molecule more than four atoms of ethylene. This latter circumstance would seem, at first, to prevent us envisaging these interesting compounds as derivatives of the ammonia type formed by substitution, but it can be explained as will be found below.

The composition of polyacids and polyalcohols shows a characteristic property: each time the divalent radical enters into their molecule, it also introduces an atom of oxygen. From that, it is natural to assume that it is this latter element that effects the bonding of the radicals. Indeed, it is easy to understand that two, three, four, or several divalent atoms or groups can, by bonding with each other, produce another divalent group. Thus, a divalent radical R" and oxygen can give the following series (27):

$$\left(\begin{matrix} R'' \\ R'' \end{matrix}\right\} \ominus \right)'' \qquad \left(R{-}^{O}{-}R \right)$$

$$\left\{\begin{matrix} R'' \\ R'' \\ R'' \end{matrix}\right\} \begin{matrix} \ominus'' \\ \ominus \end{matrix} \qquad \left.\begin{matrix} R'' \\ R'' \\ R'' \\ R'' \end{matrix}\right\}\begin{matrix}\ominus\\\ominus\\\ominus\\\ominus\end{matrix}\right\}'' \qquad \left(R\begin{matrix} O{-}R \\ O{-}R \end{matrix}\right) \qquad \left(\begin{matrix} R{-}O\ ^R \\ O\quad O \\ R{-}O{-}R \end{matrix} \right)$$

$$(R''^{n}\ominus^{n-1})'' \qquad \left(\left[O\begin{matrix} R \\ \\ R \end{matrix}\right]_n \right)$$

Again, there is an analogous case, when methylene doubles [dimerizes], triples [trimerizes], and so on, in forming homologous hydrocarbons.

$$CH^2 \quad \left\{\begin{matrix} CH^2 \\ CH^2 \end{matrix}\right. \quad \left\{\begin{matrix} CH^2 \\ CH^2 \\ CH^2 \end{matrix}\right. \quad \cdots\cdots \quad \left[n(CH^2) \right]'' \; = \; (C^n H^{2n})''$$

The general formula of the polyalcohols and polyacids, like those of ordinary alcohols and dibasic acids will thus be $\left.\begin{matrix} R'' \\ H^2 \end{matrix}\right\}\ominus^2$ and the difference will only consist of the meaning of R ″, which for the alcohols is $R^n O^{n-1}$.

Thus, one obtains, for example, the following formulas describing the chemical structure of the bodies.

ethylenic alcohol

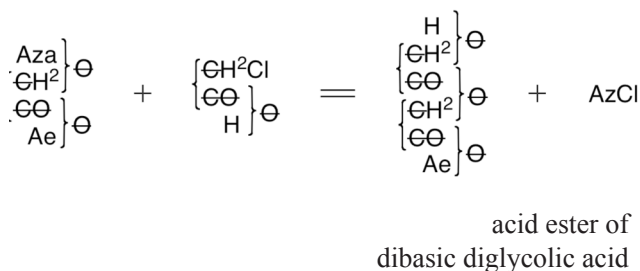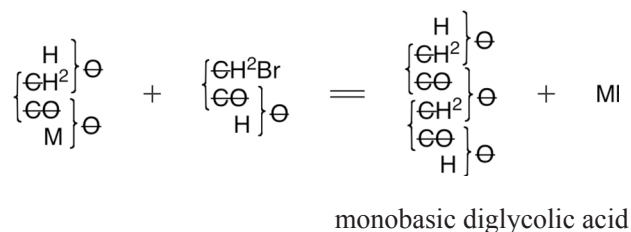$$\left.\begin{matrix} (n(C^2 H^4)\ominus^{n-1})'' \\ H^2 \end{matrix}\right\}\ominus^2$$

diglycolic alcohol

$$\left.\left(\begin{matrix} C^2 H^2\ominus \\ C^2 H^2\ominus \end{matrix}\right)''\atop H^2 \right\}\ominus^2$$

diethylenic alcohol

$$\left.\left(\begin{matrix} C^2 H^4 \\ C^2 H^4 \end{matrix}\right\}\ominus)''\atop H^2 \right\}\ominus^2$$

triethylenic alcohol

$$\left.\left[\begin{matrix} C^2 H^4 \\ C^2 H^4 \\ C^2 H^4 \end{matrix}\right.\begin{matrix}\ominus\\\ominus\\\ominus\end{matrix}\right]''\atop H^2 \right\}\ominus^2$$
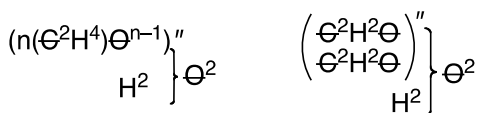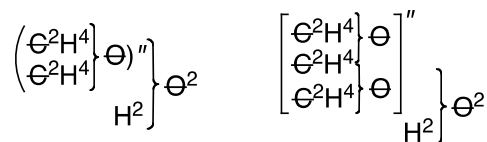
This perspective leads to the assumption that two isomeric diglycolic acids exist, of which one contains two acidic HƟ residues (bonded to carbonyl carbons), and the other one acidic HƟ residue and one alcoholic HƟ residue (combined with a saturated alkyl carbon). The second acid would have to be formed by the action of monochloroacetic acid on glycolates but since, in Mr. Heintz' experience, this reaction does not succeed, perhaps it can be obtained by the double decomposition of monobromoacetic acid or monoiodoacetic acid with glycolates. The first, already known, diglycolic acid can

doubtlessly be made in the from of the ester by the action of monochlorinated (monobrominated, monoiodinated) acetic acid on neutral monoethyl glycolate, in which the hydrogen of the alcoholic HƟ residue is replaced by sodium. The following formulas describe these reactions and the chemical structure of the two diglycolic acids (28).

$$\left.\begin{matrix} H \\ CH^2 \\ CO \\ M \end{matrix}\right\}\begin{matrix}\ominus\\\\\ominus\end{matrix} \;+\; \left.\begin{matrix} CH^2Br \\ CO \\ H \end{matrix}\right\}\ominus \;=\; \left.\begin{matrix} H \\ CH^2 \\ CO \\ CH^2 \\ CO \\ H \end{matrix}\right\}\begin{matrix}\ominus\\\\\ominus\\\\\ominus\end{matrix} \;+\; MI$$

monobasic diglycolic acid

$$\left.\begin{matrix} Aza \\ CH^2 \\ CO \\ Ae \end{matrix}\right\}\begin{matrix}\ominus\\\\\ominus\end{matrix} \;+\; \left.\begin{matrix} CH^2Cl \\ CO \\ H \end{matrix}\right\}\ominus \;=\; \left.\begin{matrix} H \\ CH^2 \\ CO \\ CH^2 \\ CO \\ Ae \end{matrix}\right\}\begin{matrix}\ominus\\\\\ominus\\\\\ominus\end{matrix} \;+\; AzCl$$
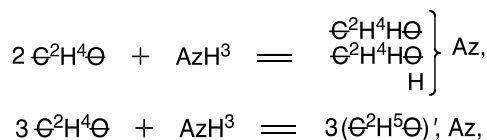
acid ester of
dibasic diglycolic acid

It is clear that the divalent compound radical $(R^n)''(O^{n-1})''$ acts in most cases like a simple divalent radical, and can also give derivatives of the ammonia type. It is also known that a divalent group becomes monovalent itself when it bonds to a monovalent group. This explains the formation of Mr. Wurtz' oxygenated bases and leads to the assumption of a crowd of isomeric compounds. In the reaction of ethylene oxide and ammonia, the hydrogen of the latter substance combines with the oxygen of the former, forming the HƟ residue, and this, on bonding to divalent ethylene, gives the monovalent ethyl oxide $(C^2 H^5\ominus)'$, which remains bonded to the ammoniacal residue, producing the base

$$C^2 H^4\ominus \;+\; AzH^3 \;=\; \left.\begin{matrix} C^2 H^{4\,\prime}H\ominus' \\ H \\ H \end{matrix}\right\} Az$$
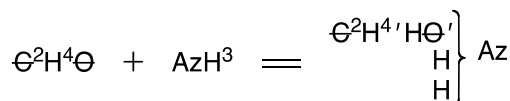
As far as the presence of the hydroxyl hydrogen (of the residue HƟ) in these bases is concerned, that has been put beyond doubt by the research of Mr. A. Hofmann.

The formation of secondary and tertiary amines, etc., is therefore explained in a completely analogous way (29).

$$2\,C^2 H^4\ominus \;+\; AzH^3 \;=\; \left.\begin{matrix} C^2 H^4 H\ominus \\ C^2 H^4 H\ominus \\ H \end{matrix}\right\} Az,$$

$$3\,C^2 H^4\ominus \;+\; AzH^3 \;=\; 3(C^2 H^5\ominus)',\,Az,$$

$$4\,C^2H^4O \;+\; AzH^3 \;+\; H^2O \;=\; 4\,(C^2H^4,HO)'Az\!\Big]\!O$$
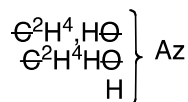
In every case, the carbon groups are bonded into a single molecule by the chemical combining power of the nitrogen, but they can also, as seen above, be bonded
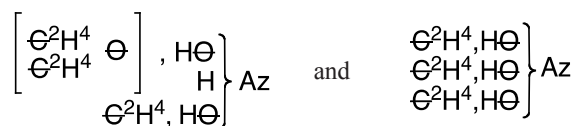
$$\begin{bmatrix} C^2H^4 \\ C^2H^4 \end{bmatrix}\!O \;\left|\begin{matrix} HO \\ H \\ H \end{matrix}\right\}Az$$
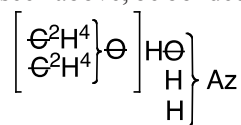
through oxygen. Thus, an amine

$$\begin{matrix} C^2H^4,HO \\ C^2H^4HO \\ H \end{matrix}\right\}Az$$

metameric with the amine must also exist. The second of these bases is the secondary amine (an imide base) from glycol when it acts as a monoatomic alcohol

$$(C^2H^4,HO)'\!\Big\}O$$
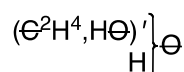
while the first is the primary amine from diethylene alcohol. Likewise, the following two metameric substances must also exist:

$$\begin{bmatrix} C^2H^4 \\ C^2H^4 \end{bmatrix}\!O\;\left|\,\begin{matrix} HO \\ H \end{matrix}\right\}Az \qquad \text{and} \qquad \begin{matrix} C^2H^4,HO \\ C^2H^4,HO \\ C^2H^4,HO \end{matrix}\right\}Az$$

The subsequent application of this view is easy, and the isomeric amines that appear in limitless number are distinguished from each other by the amount of hydrogen directly bonded to the nitrogen (ammonia-type hydrogen). One should be able to easily recognize their nature by preparing, for example, their methyl derivatives. The HO residue in the alcohol cannot be substituted by the direct action of the iodide—that is beyond doubt. It can probably be replaced by means of an indirect method, by substituting sodium for the hydrogen of the residue, and treating the sodium alkoxide with the iodide. It can equally well be replaced by the reaction of a sodium alkoxide with a derivative of the base containing a halogen group in place of the HO residue whose hydrogen one wants to replace.

The polyamide acids should give similar results. Designating the glycolyl radical (C^2H^2O) (30) by Gl, for example, one obtains the following metameric species:

I.

$$\left.\begin{matrix} (Gl,\,HO)' \\ (Gl,\,HO)' \\ H \end{matrix}\right\}Az$$

and

II.

$$\left[\left(\begin{matrix} Gl \\ Gl \end{matrix}\right)''HO\right]'\!\left.\begin{matrix} \\ H \\ H \end{matrix}\right\}Az$$

or

III.

$$\left.\begin{matrix} (Gl,\,HO)' \\ (Gl,\,HO)' \\ (Gl,\,HO)' \end{matrix}\right\}Az$$

IV.

$$\left[\left(\begin{matrix} Gl \\ Gl \end{matrix}\right)''HO\right]'\!\left.\begin{matrix} \\ (Gl,\,HO)' \\ H \end{matrix}\right\}Az$$

V.

and

$$\left[\begin{matrix} Gl \\ Gl \end{matrix}\right\}O\right]''\!\left.\begin{matrix} ,HO)' \\ H \\ H \end{matrix}\right\}Az$$
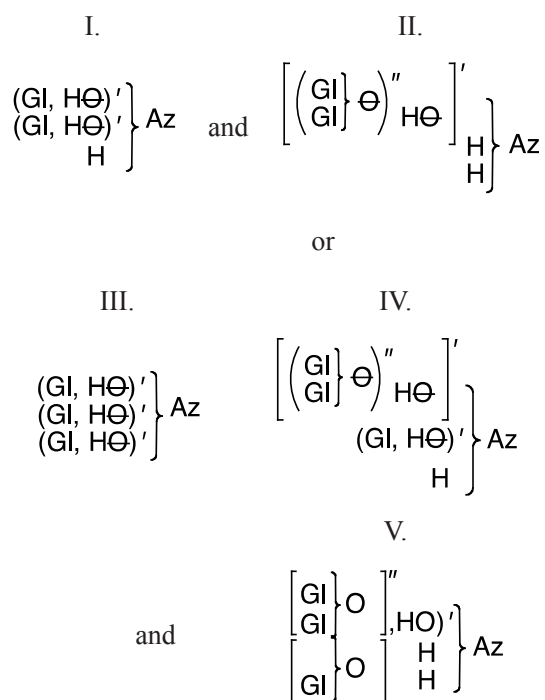
Formulas (I) and (III) represent the di- and tri-amidic acids of Mr. Heintz, which are, in all probability, secondary and tertiary monoamines. Formulas (II and V) belong to the class of primary amines, which are to diglycolic and triglycolic acid as glycine is to glycolic acid. Finally, the amide acid described by the formula (IV) is a secondary amine containing a compound residue of diglycolic acid and a simple glycolic acid residue. By the action of nitrous acid, this last compound would possibly give diglycolic acid and glycolic acid at the same time.

May these considerations lead to experiments in the direction that they indicate!

References and Notes

1. Kolbe, *Lehrbuch*, vol. 1, p. 23.

2. Gerhardt, *Traité*, vol. IV, p. 561.

3. Kekulé, *Lehrbuch*, vol. I, p. 61.

4. Kolbe, *Lehrbuch*, vol. I, p. 13. See also vol. II, p. 576.

5. Gerhardt, *Traité*, vol. IV, p. 573.

6. Kekulé, *Lehrbuch*, vol. 1, p. 157.

7. Kekulé, *Lehrbuch*, vol. I, p. 164 and 161; see also vol. II, p. 6 and 7.

8. This word already appears to describe the position of the atoms in space, which is in contradiction to the ideas that one finds a little earlier in the same work (vol. I, p. 157 and 162).

9. *The topographical position of the atoms*, an expression that has also been used lately, appears to me to be less suitable because it implies the idea of determining the position of the atoms in space. Speaking of the ratio of the atoms in a molecule, one need not know their positions, nor even admit the existence of physical atoms. Only in the case where the hypothesis of the existence of these last would be absolutely necessary for a chemist, would one have the right to assert that the considerations of Mr. Kolbe constitute an attempt to determine the position of the atoms in space. Since the hypothesis of physical atoms has not yet become essential for our science, and since certain chemists do not admit the possibility of determining their position, each expression that implies this hypothesis and this possibility will only delay the time when the different theoretical views will be merged into one.

10. Kekulé, *Lehrbuch*, vol. I, p. 158.

11. Kekulé, *Lehrbuch*, vol. I, p. 177; vol. I, p, 95 and 96.

12. Kekulé, *Lehrbuch*, vol. I, p. 556.

13. [The carbon is shown here with a bar, presumably as Butlerov intended. In the original, the bar is missing, presumably a printing error. —DEL]

14. Kekulé, *Lehrbuch*, vol. II, p. 2.

15. Kolbe, *Lehrbuch*, vol. I, p. 742.

16. This perspective has led Mr. Kolbe to express opinions that will never be reconciled with theoretical ideas of valence. In his paper on the isomerism of fumaric and maleic acids, etc., for example, he notes that carbon is not only a di- and tetravalent atom, but also trivalent. He views the composition of oxalic acid, $2OH,C^4O^6$, as a proof of this trivalency. He loses sight of the reason why the two carbon atoms (the two carbonyls of Mr. Kolbe) are linked together, and which is certainly nothing other than the action of a quarter of the chemical combining power belonging to each atom of that element, and holding these atoms [together] not only in oxalic acid, but also in ethyl hydride, alcohol, glycol, etc. It is certainly correct to state that the carbon group $2C^{IV}$ is hexavalent, but not to deduce from that that the carbon itself is a trivalent atom. By rigorously following Mr. Kolbe's view, one would have to accept that carbon has a valence of 2 2/3 in mesoxalic acid and propyl hydride, of 2 1/2 in butyl hydride, monovalent in phenyl hydride, and so forth. It should be pointed out at the same time, that Mr. Kolbe's idea on the state of nitrogen in Mr. Griess' substances is not new to me. More than a year ago, I expressed it in my paper, "On amines," (in the Russian language, in the writings of Kazan University). There I gave the following parallel:

$$C^7H^6O^2 \qquad C^7H^5(H^2Az)'O \qquad C^7H^4(\overset{'''}{A}z\overset{'''}{A}z)''O^2$$

| benzoic acid	amidobenzoic acid	azobenzoic acid
	[benzamide]	[4-carboxyphenyl-diazonium]
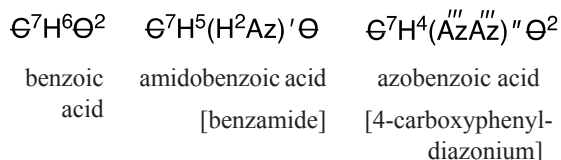
and I pointed out the way in which the substances in question form, which consists of the substitution of an atom of nitrogen by three atoms of hydrogen (of which two are bonded to the nitrogen), and gives some probability to this hypothesis.

17. Vol. I, p. 157.

18. The formation of ethylene and ethylidene oxide (acetaldehyde) can be explained by the loss of hydrogen atoms belonging to different carbon atoms in alcohol.
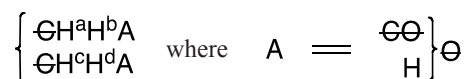
$$\begin{Bmatrix} CH^3 \\ CH^2 \\ H \end{Bmatrix}O \;-\; H^2 \;=\; \begin{Bmatrix} CH^3 \\ CH,O \end{Bmatrix} \quad \text{(acetaldehyde)}$$

$$\begin{Bmatrix} CH^3 \\ CH^2 \\ H \end{Bmatrix}O \;-\; H^2O \;=\; \begin{Bmatrix} CH^2 \\ CH^2 \end{Bmatrix} \quad \text{(olefiant gas)}$$
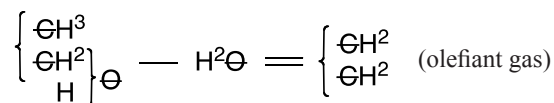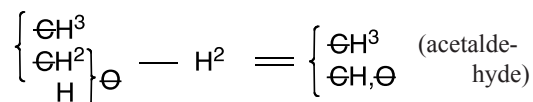
19. [The first of these structures has an extra hydrogen atom in the original, appearing as

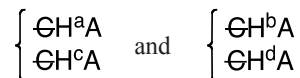$$\begin{Bmatrix} CH^2Br \\ CHBr \end{Bmatrix} \text{. —DEL]}$$
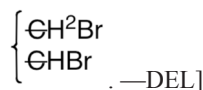
20. [Butlerov's logic here predicts that both the Kekulé and Kolbe structures will give two isomeric dibromides, but it is equally clear that they do not predict the same two structures. Here, Butlerov does not appear to be willing to endorse one set of structures over the other—perhaps because he could not deduce a method to distinguish between them. —DEL]

21. I find it difficult to understand why Mr. Erlenmeyer accepts that the hydrogen lost from succinic acid comes from each of two different carbon atoms (*Zeitschrift für Chemie und Pharmacie*, **1863**, p. 22). This point of view assumes that the hydrogen contained in ethylene are different; if all four hydrogen atoms of olefiant gas were different, one would have to have 4 isomers $C^4H^4O^4$. Indeed, if succinic acid is expressed by the formula
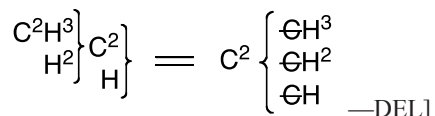
$$\begin{Bmatrix} CH^aH^bA \\ CH^cH^dA \end{Bmatrix} \quad \text{where} \quad A = \begin{Bmatrix} CO \\ H \end{Bmatrix}O$$

one can clearly see that the bodies

$$\begin{Bmatrix} CH^aA \\ CH^cA \end{Bmatrix} \quad \text{and} \quad \begin{Bmatrix} CH^bA \\ CH^dA \end{Bmatrix}$$
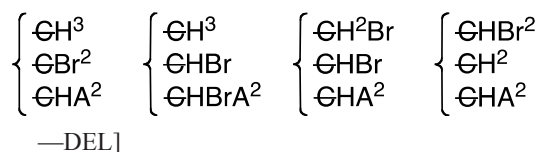
must be identical if all the hydrogen atoms are identical, and that it is possible for 4 isomers of $C^4H^4O^4$ to exist if

all the atoms of this element are different.

22. [There is clearly an error in this formula, with the "C²" and "=" symbols being transposed. The corrected version has been used in the translation. The original publication contains the following:
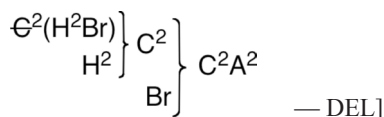
$$\left.\begin{array}{l} C^2H^3 \\ H^2 \end{array}\right\}C^2\left.\begin{array}{l} \\ H \end{array}\right\} \;=\; C^2\left\{\begin{array}{l} \cancel{C}H^3 \\ \cancel{C}H^2 \\ \cancel{C}H \end{array}\right. \quad —DEL]$$

23. [There are clearly errors in the left-hand pair of acids, with the second structure containing a formally pentavalent carbon. The corrected version of the set has been used in the translation. The original publication contains the following:

$$\left\{\begin{array}{l}\cancel{C}H^3 \\ \cancel{C}Br^2 \\ \cancel{C}HA^2\end{array}\right. \quad \left\{\begin{array}{l}\cancel{C}H^3 \\ \cancel{C}HBr \\ \cancel{C}HBrA^2\end{array}\right. \quad \left\{\begin{array}{l}\cancel{C}H^2Br \\ \cancel{C}HBr \\ \cancel{C}HA^2\end{array}\right. \quad \left\{\begin{array}{l}\cancel{C}HBr^2 \\ \cancel{C}H^2 \\ \cancel{C}HA^2\end{array}\right.$$

—DEL]

24. [The printed version places the dibrominated and unsaturated acid structures on the same line in such a way that it is not clear that there are two separate structures. In addition, the dibrominated structure, shown below,

includes a barred carbon atom (C), which is not part of Kolbe's notation:

$$\left.\begin{array}{l}\cancel{C}^2(H^2Br) \\ H^2 \end{array}\right\}C^2\left.\begin{array}{l} \\ \\ Br\end{array}\right\} C^2A^2$$

— DEL]

25. *Lehrbuch*, Vol. II, p. 587.

26. [These compounds are known today as nitrilodiacetic acid, and nitrilotrioacetic acid, respectively. —DEL]

27. [The structures on the right are "translations" of Butlerov's structures into modern notation. —DEL]

28. If I use these types of formulas here and above to describe the chemical structure, it is because these formulas resemble the type formulas to which we are generally accustomed.

29. [The first of these structures was misprinted in the original, as shown below; the oxygens in the product were not barred.

$$2\;\cancel{C}^2H^4\cancel{O}\;+\;AzH^3\;==\;\left.\begin{array}{l}\cancel{C}^2H^4HO \\ \cancel{C}^2H^4HO \\ H\end{array}\right\}Az$$
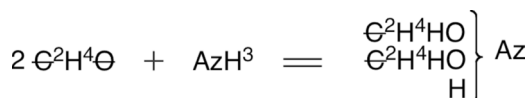
—DEL]

30. [This corresponds to the modern structure –CH₂CO–. —DEL]

WHY ISN'T NOBLE GAS CHEMISTRY 30 YEARS OLDER? THE FAILED (?) 1933 EXPERIMENT OF YOST AND KAYE

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Introduction

We know of a number of unsuccessful attempts to synthesize a noble gas compound (1)—probably there were others of which we do *not* know—that preceded the first announcement by Neil Bartlett in 1962 (2), now a little over half a century old. Perhaps the best documented of these was reported in a 1933 paper in *JACS*—a relatively rare instance of publishing of a negative finding!—by Caltech chemistry professor Donald M. Yost and his graduate student Albert L. Kaye (3). After Bartlett's success, which was quickly followed by others, Yost's failure became a subject of some interest, probably due in part to the significant role of Linus Pauling. A variety of explanations have been offered for why Yost was unable to generate any compound of xenon with fluorine—or, perhaps, that he *did* generate something but failed to recognize it. But these would-be explainers appear to have relied mostly on their *recollection* of what Yost and others did; and in many cases that recollection was faulty. Examination of the actual details of Yost's paper, in comparison with those of the later successful reports, shows that the subsequent interpretation by a number of commentators—researchers, reviewers, biographers—has been imprecise, unsupported, or just plain wrong. On the other hand, one particular detail of Yost's experiment, which appears to have gone completely unnoticed, offers a plausible explanation for why Yost did not— though he could well have—beat Bartlett and his contemporaries by nearly 30 years.

Linus Pauling, Before and After Yost's Experiment

Unquestionably Pauling instigated Yost's work. According to one of Pauling's biographers (4):

> One daring prediction Pauling made was that fluorine was so electronegative it would form compounds even with an inert gas like xenon…. Pauling managed to obtain a little of it from a colleague and gave it to Yost, who worked through the summer of 1933 searching for the predicted compounds. He failed to find any—a failure that Pauling found both confusing and galling. The reasons for Yost's inability to find what he was looking for are uncertain.

Note that Hager, unlike other commentators, is (deliberately?) agnostic with regard to the reasons for the failure. But his facts are well documented. In particular, we have three letters from Pauling to Fred Allen, one of Pauling's former professors who had moved to Purdue, and who possessed a modest supply of xenon. The first requests the loan of a sample (5):

> I should like to do some work (with Professor Yost) in an attempt to prepare certain compounds of Xenon suggested by theoretical arguments. No doubt your xenon is precious; if, however, you could lend us 10 cc. or so (of not necessarily pure stuff), we would try to return it to you either as such or in some compound (I hope), and we would be properly grateful. If this is asking too much, or if you can't lend it, could you give us advice as to where we might possibly obtain some?

while the second (6) and third (7) report the unhappy results:

> At last I can send you some information regarding the xenon experiments, which Dr. Yost has been carrying on, inasmuch as he is thoroughly experienced in the chemistry of the halogens. He found that he could not prepare a compound of xenon with either chlorine or fluorine by any of the means that he tried, and he has now given up the investigation. He and his student, Kaye, have sent a note on the experiments to the Journal of the American Chemical Society, in which they thank you for providing the xenon, I am sorry that the experiments have turned out in this way since I felt confident that xenon would combine with fluorine, at any rate, Yost obtained some red crystals, which he at one time thought contained xenon, but which he later decided were the pink form of hydrogen chloride.

> The 70 mm of xenon was the pressure in mm of mercury, the volume of the system being 300 or 400 cc. Hence there was plenty of xenon present. Yost should have mentioned the volume. We still have the xenon, but Yost would like to make another try at preparing a compound (unless you want the xenon returned soon). I still think XF_6 [*sic*] should be stable.

Why did Pauling turn to Yost (and Kaye) to test his rather revolutionary idea? Yost (Figure 1) was a (self-described) physical inorganic chemist—indeed, the only inorganic chemist at Caltech at the time—who had considerable experience in (and taste for) gas-phase experimentation with difficult materials, such as chalcogen halides (8) and interhalogen compounds (9); in contrast, Pauling's work at the time (and subsequently) was virtually exclusively

Figure 1. *Don Yost, photograph taken in 1948. Courtesy of the Archives, California Institute of Technology.*

devoted to theory and structural determinations. They had already co-authored one paper, on electronegativity and ionic contributions to covalent bond strengths (10), although the paper reads very much like entirely Pauling's ideas, with Yost contributing only some interhalogen bond energy data. To propose a collaboration must have seemed obvious to Pauling.

Albert Kaye arrived at Caltech in September 1932 to begin work on a Ph.D. in *physics*, but apparently chose to work with Yost, a professor in a different department. (Such freedom is still available to Caltech graduate students.) The *JACS* paper with Yost is the only extant record of his time at Caltech (he also appears as a co-author on several papers on electrochemistry with MIT professor M. de K. Thompson, the earliest dating from 1932; presumably these arose from his undergraduate research); there was no thesis, and he left Caltech after just one year (11). I have not been able to find out anything about his subsequent career.

A couple of years after Bartlett and others opened up the field of noble gas chemistry, Pauling reminisced about the failure in the course of a lecture (12)

> I think it's good to be skeptical about a lot of things. This xenon business was a lesson to me but I don't know just what it taught me. [laughter] In 1932, I think it was, I said that it ought to be possible to make xenon hexafluoride XeF_6, to make a hydroxy compound $Ag_2H_3XeO_6$. This has been made, by the way, these compounds have been made -- Professor Yost and a student name Kaye, Albert Kaye. It was hard to get Xenon in those days. My early teacher of physical chemistry of Corvallis had some xenon which he sent to us -- a couple of hundred of milliliters of the gas and it may be that Yost and Kaye really had some xenon fluoride but just failed to observe that they had that when they did this work in '33 and '34.

and again, still later (and with considerably more evident bitterness) during an interview archived at the Chemical Heritage Foundation (13)

> Freddy [Allen] sent me about 200 milliliters of gaseous xenon for the experiment. I wasn't the experimenter. I got Don Yost to try to make it, and he reported that he didn't succeed. He had a nickel apparatus, and he couldn't see inside it. The man who later made the xenon compounds … said he was sure that Yost had made xenon difluoride, but had failed to recognize that he had. I think he may have been measuring the change in pressure but I don't remember just how the experiment was carried out. So Yost reported in a paper that you couldn't make xenon fluoride…. Someone at CIT said that he thought this was about the most unenthusiastic investigator who ever carried out an investigation. I judge that Don did this just because I asked him to, but perhaps he was convinced that it would be a failure.

Several points should be noted: the possibility, offered as Pauling's own opinion in the first quote and
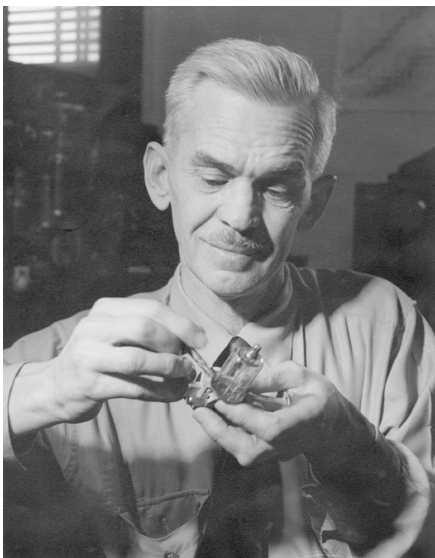
attributed to Bartlett in the second, that Yost *had* made XeF_2 but didn't realize it; Pauling's memory—although he acknowledges almost immediately that his memory is unclear—of Yost's having done the experiment in an opaque nickel apparatus; the suggestion by "someone" at Caltech that Yost had never been really committed to the effort and might have been predisposed to failing; and Yost's conclusion (per Pauling) that xenon fluoride could not be made.

Bartlett and Other Commentators

Neil Bartlett spoke at length about Yost's experiment, long after his own discoveries, in the course of a 1999 interview (14):

> Linus was so convinced that there should be some xenon chemistry that he wrote his old teacher Fred Allen, at Purdue, and begged from him a sample of xenon. It was difficult to get samples of xenon in those days. Linus then took xenon to his Caltech colleague Don Yost, who had a student, Kaye, and Yost and Kaye put xenon and fluorine into a quartz bulb. Then they made a mistake. They should have gone out into the Caltech sunlight. Instead, they passed an electric discharge through the bulb and all they got was attack on the quartz container. Quartz is not very resistant to fluorine…. They reported this in the *Journal of the American Chemical Society* in 1933 in a paper on the nonreactivity of xenon with fluorine. That, I suppose, persuaded Pauling that he had been a little too optimistic. The xenon fluorides are close to the limit of thermodynamic stability, after all, and accessible xenon chemistry depends upon that slight stability….
>
> [Hargittai: How did Pauling react, 30 years later, to your discovery?]
>
> He was informed very early on by myself. His reaction was that Yost and Kaye had distinctly missed the boat. He, Pauling, had made the right prediction. Of course, Yost could have suggested to Linus to try it for himself. I never met Don Yost but he writes in an engaging and amusing way. He must have been quite a character…. What we do with fluorine today is done at room temperature by just using photons to dissociate the fluorine. Everything is done in fluorocarbon plastic…. Such containers did not exist in Don Yost's days. He was working in quartz because he knew well that fluorine is extremely difficult to handle in ordinary glass. You could use Pyrex if you got it really dry. Yost probably didn't know that and he probably had some HF in his fluorine.

Bartlett's recollections differ significantly from Pauling's (as well as being much more detailed; it seems likely that

he refreshed his memory by reference to Yost's paper shortly before, or even during, the course of the interviews!), particularly with regard to the reaction vessel: quartz according to Bartlett whereas Pauling remembered (incorrectly, as we shall see) nickel. There is no suggestion of a poor attitude on Yost's part (of course, Bartlett never knew Yost personally, unlike Pauling), nor that he believed (as Pauling says) that Yost had unknowingly made XeF_2. Bartlett attributes the failure to two "mistakes": the use of a quartz apparatus, and the choice of electric discharge rather than photochemical activation.

The latter argument had already been offered in an earlier review (15):

> Others also thought of attempting combination of halogens with noble gases in the 1930s, among them Pauling. He was convinced that xenon and fluorine, at least, should react and, at his suggestion, Yost and Kaye tried a discharge experiment. Their failure to gain a definitive result was cruelly unfortunate since, exposure of xenon-fluorine mixtures to sunlight instead of electric discharge, when tried some 30 years later, produced XeF_2.

There is an intriguing but unresolved aspect of this quote: did Pauling specifically suggest the discharge method—a mistake, according to Holloway and Bartlett—or just the attempt, leaving the choice of method to Yost? I have not found any support for the former interpretation, or any indication of why Holloway might have said that, if that is indeed what he meant. In any case, as we shall see shortly, it is far from clear that it *was* the wrong choice, no matter who made it.

John Waugh, one of Yost's last graduate students (and by far the best-known, for his subsequent career in NMR), addressed the episode as part of a biography of Yost that he provided for the National Academy of Sciences (16):

> The chemistry of rare or "difficult" elements was always a challenge to Yost. Fluorine chemistry was no exception. Indeed, Yost earned an international reputation for his work on the volatile inorganic halides. Apparently the notion arose in the early 1930s (probably from Linus Pauling) that xenon, a "noble gas" guaranteed by all the textbooks to be chemically inert, might form chemical compounds with fluorine, the most electronegative element. Yost (who would not have used the word electronegative) and Albert L. Kaye describe in a 1933 paper a failed attempt to prepare such compounds. Neil Bartlett, who won fame many years later for preparing xenon fluorides, considers it nearly certain that such compounds must

have been created under the conditions used by Yost and Kaye. We can only speculate on the reasons for their negative result on an experiment which might have had a revolutionary effect.

As we have seen, credit for the inspiration definitely, not "probably," belongs to Pauling. The comment about Yost's attitude towards electronegativity is interesting in light of a paper he co-authored with Pauling (10), which is thoroughly imbued with the concept; while Yost may well have contributed little to the actual writing, as I suggested, at least at that time he was willing to put his name to an article centered thereupon. I suspect that his strong antipathy—if Waugh is correct about that—developed subsequently, not out of any scientific commitment but more from his personal feelings about Pauling, which will be discussed shortly.

Like Pauling's biographer Hager, Waugh is here rather circumspect about possible causes for the failure; but in his later personal memoir he permitted himself somewhat more speculation (17):

> I signed up for research with Don Yost, who was a colorful and crusty character, and a man of catholic interests…. In 1933, at Pauling's instigation, Yost and A. L. Kaye had tried to make xenon halides but failed. That may have been because Yost did not like Pauling very well; Neil Bartlett once told me that Yost's experiment must have created xenon compounds.

Again we have a statement that Bartlett believed Yost had in fact succeeded, although Bartlett himself says no such thing in his interview. More importantly, this is the strongest suggestion that Yost's relationship with Pauling could have contributed to his failure.

Lastly, what did Yost himself have to say? There is a huge collection of Yost's papers in the Caltech archives but, unfortunately, they only date back to around 1940, so there is no contemporaneous documentation, and no commentary in any of his later personal papers. He did write a brief introductory article (18) to a 1963 monograph, a collection of articles on the then-new field of noble gas chemistry, which included the following:

> My sole excuse for being a contributor to this important book rests in the fact that, as mentioned above, Albert Kaye, then a graduate student, and I tried without success to bring about reaction between xenon and both chlorine and fluorine…. We were on our own throughout. We constructed our own apparatus, blew our own glass, and used cast off Ford coils as a source of high potentials…. Our sole supply of xenon was some 200 cc. at less than one-half atmosphere pressure which had been kindly loaned to us by Dr. Fredrick John Allen of Purdue. Furthermore, we had

> to construct and operate our own (temperamental) fluorine generator…. The techniques (or art) of handling fluorine and its generators were in primitive stages of development…. There may, of course, be serpents who will say, and possibly with some reason, that if in spite of undeveloped techniques we had worked harder and more exhaustively we would have succeeded in preparing one or more xenon fluorides. But the simple fact is that we didn't succeed…. Mr. Kaye and I will have to rest content with the fringe virtue of having said in print that we hadn't proved by our experiments that a xenon fluoride was incapable of existing.

One can't help noticing the absence of any mention of Pauling: in Yost's account the xenon was loaned to "us," not Pauling. By this time Yost could hardly bring himself to use Pauling's name, often using phrases such as "the unnamed person (19)." (Actually Pauling probably *is* mentioned, in a way: I have little doubt that "serpent" was intended to refer to him.) But aside from that, Yost notes (correctly) that the paper explicitly left open the possibility of the existence of xenon compounds, whereas Pauling's reminiscences (see above) implied Yost had concluded they could *not* be made. Yost puts his failure down to "undeveloped techniques," particularly, it would seem, the difficulty of working with F_2.

Yost and Pauling

Is there any support for the suggestion, made most explicitly by Waugh but also detectable in other commentaries, that the personal relationship between Yost and Pauling played any causal role in Yost's failure? There is no question that Yost and Pauling developed an intense dislike for one another at some point in time, as I have documented, based on the Yost archives (19). Hager suggests it began when Pauling assumed the chairmanship in 1937, and began to favor his own field of structural chemistry as well as biochemistry at the expense of physical and inorganic chemistry, although the discord may well have been exacerbated when Bartlett's discovery reawakened Pauling's memory of Yost's failed effort (20):

> Don Yost, a highly opinionated, individualistic inorganic chemist, became "somewhat antagonistic to me," Pauling remembered, in part because of his unhappiness at the shift in emphasis away from his field and perhaps in part because of lingering bad feelings over a fiasco in which Yost failed to find the xenon compounds that Pauling had predicted should exist. Yost stayed at Caltech until he retired, often at loggerheads with Pauling, the sole dissenting vote

in many divisional decisions, his rancor barely concealed and growing to the point where he and Pauling sometimes stopped speaking to each other entirely.

The antagonism was full-blown by the 1940s—and was surely not all one-sided, as Hager's quote might imply: Pauling completely, and clearly deliberately, omitted Yost from a listing of chemistry faculty in a 1944 memo (19). Yost later returned the favor when in 1958, after Pauling had left Caltech, his successor as chair, Ernest Swift, requested a historical summary of "Departmental Accomplishments" from each faculty member. Yost provided a list (21) of some 14 areas of excellence and 20 or so names, with Pauling left out entirely—except for the sentence, "There are reptiles who would induce us to believe that Chemistry was devoted chiefly to molecular structure," a clear allusion to the unnamed enemy (see "serpent" above).

But there is no evidence that I can find of hostility dating as far back as 1932-33. The only significant earlier reference to Yost in the Pauling archives is in a 1931 letter to John Slater, declining an invitation to move to MIT (22):

> If I were to come to M.I.T., I should desire an appointment in physics or in physics and chemistry. And yet I am really not very much interested in physics, but rather in what may be called structural chemistry, and so I prefer being in a chemistry department. Here there are several men in our chemistry department whose interests touch on mine—Tolman, Badger, Dickinson, and Yost especially.

That certainly *sounds* as though they still got along well enough in 1931. When we also consider the co-authored paper of 1932 and, not least, that Pauling turned to Yost to try his great xenon idea and that Yost (apparently) readily agreed, it is hard to see any justification for including a personal factor in accounting for the failure.

What Yost (and Others) Really Did

If we rule out the personal factor, Yost's failure would have to be ascribed to one or more technical deficiencies or errors. As we've seen, the various suggestions offered—wrong materials, use of discharge instead of light, impure reagents—were often based on fuzzy and even contradictory recollections of the actual experiments done by Yost, as well as the successful ones that followed Bartlett's breakthrough. What are the facts?

Yost and Kaye's first attempts were with Cl_2; most probably it was more readily available than F_2. That work was carried out *both* in quartz and in Pyrex, and they tried *both* light and electric discharge to initiate reaction. Not surprisingly (from what we now know), nothing happened (except for formation of a small amount of the colored modification of HCl mentioned by Pauling) (3):

> A mixture of xenon (70 mm.) and chlorine (225 mm.) contained in a quartz tube was irradiated with the light from a mercury arc in Pyrex and in quartz, and from a carbon arc…. In no case was any pressure change observed…. The mixture was next transferred to a Pyrex bulb equipped with tungsten electrodes. After sparking for varying periods of time and then condensing the contents of the bulb … the red solid noted above appeared…. No definite evidence for the presence of a xenon chloride was found.

They then turned to fluorine; but here they worked *only* in quartz, not Pyrex, and with electric discharge, *not* with light (3):

> It was found that fluorine, carefully freed from hydrogen fluoride, could be kept for an indefinite period in quartz bulbs which had been baked out under vacuum…. A mixture of some 600 mm. of fluorine and 30 mm. of xenon was prepared in an all-quartz apparatus provided with copper electrodes…. A high voltage (30 k.v.) discharge was then passed through the mixed gases for varying intervals of time. The contents of the apparatus were condensed out frequently, but the appearance and properties were no different from those observed before applying the discharge. It was noted that the side tube was appreciably attacked after some time, and this might be due to the action of a reactive xenon fluoride…. It cannot be said that definite evidence for compound formation was found. It does not follow, of course, that xenon fluoride is incapable of existing.

In hindsight, it seems strange that Yost and Kaye used a wider range of experimental conditions with chlorine than fluorine. Yost surely understood (for example, from his joint paper with Pauling (10)) that a fluoride was much more likely to be stable. It is true that preparing the F_2 sample entailed more work; but the Cl_2 experiments were all done on a single preparation of mixed gases, so that shouldn't have been an issue. Why did they use only quartz? Bartlett's suggestion, that Yost didn't realize fluorine could be handled safely in Pyrex, seems reasonable. More importantly, why didn't they try light irradiation? I can only surmise that the fact that F_2 is colorless, unlike Cl_2, might have made them think that photochemistry would be less apt to succeed with the former.

Whatever the reasons, the narrative *up to this point* appears consistent with blaming the choice of electric discharge rather than light as the prime cause for failure, as did Bartlett and Holloway. Formation of XeF_2 from Xe

and F_2 under the action of light from a mercury arc lamp was reported shortly after Bartlett's initial paper (23). A couple of years later the experiment that Bartlett said Yost *should* have tried—exposure to ambient sunlight (and in Pyrex, to boot)—also succeeded (24). Bartlett's further suggestion, that the choice of a quartz vessel and the possible presence of HF could have also been problematic, is likewise not inconsistent.

However, there is one more piece of the story that refutes all of that! Bartlett and Holloway apparently had forgotten (or never realized?) that the *first* (25) reported preparation of XeF_2, by Hoppe and coworkers (26), was achieved using Yost and Kaye's methodology:

> Commercial xenon … was mixed with carefully purified fluorine (prepared electrolytically) in a $Xe{:}F_2$ proportion of 1:2 by volume in a sealed quartz vessel and subjected at room temperature to discharges from an induction coil…. After a short interval, a fall in pressure occurred, after several (up to 10) hours, it corresponded at maximum to a 50% decrease in volume of the original quantity of gas. Simultaneously a colorless crystalline condensate was formed on a cold finger…. The analytical data show that its overall composition corresponds approximately to the empirical formula XeF_2.

As can be seen, Hoppe used activation by discharge, not light; he worked in a quartz apparatus, not Pyrex; he used home-made F_2, not a commercial sample; and he monitored the reaction by attempting to condense out product. All of that is (almost: see below) *exactly* what Yost and Kaye tried (27)! Clearly, then, most of the prior explanations are *not* correct: the "mistakes" cited—failure to use light, working in quartz—were not mistakes at all. As for the possible presence of HF, Yost and Kaye explicitly comment that they "carefully" removed it, and there is no reason to believe they were less capable than Hoppe in this regard. Furthermore, if any appreciable amount of HF *had* been present, attack on the vessel walls should have been visible from the very beginning of the experiment, not just "after some time."

So what *was* the key difference between Hoppe's success and Yost's failure? Only one is apparent: the composition of the gas mixture. Hoppe used 1:2 $Xe{:}F_2$, at a total pressure around 1 atm (26), corresponding to partial pressures of Xe and F_2 around 250 mm and 500 mm, respectively. That's fairly typical of other contemporary studies: for example, Streng and Streng used 350 mm Xe and 374 mm F_2, around 1:1 (24). In contrast, Yost and Kaye used 30 mm and 600 mm: more F_2 and *much* less Xe, a ratio of 1:20.

Again, we may wonder why they made that choice, especially given that making the F_2 was a major challenge; note (see above) that they used a good deal more Xe and less halogen for the chlorine experiment, 70 mm and 225 mm respectively. Could they have been influenced by Pauling here? Recall that he had predicted XeF_6 as his expected product.

But the central question is, could this have made a major difference? Almost certainly so. The mechanism of the reaction of Xe with F_2 is complex, but studies agree that the reaction begins with dissociation of F_2 to 2 F•, with the latter adding to Xe to form FXe•; there are several ways to go on from there (28,29). Assume that the electric discharge method generates radicals at a given rate; that the rate is similar between Yost's and Hoppe's work (of course we can't know for certain just how the experimental setups compare in this regard); and that the following (much oversimplified) discharge-initiated chain mechanism operates:

$$F_2 \underset{\longleftarrow}{\overset{\text{energy}}{\longrightarrow}} 2\ F\bullet$$

$$F\bullet + Xe \longrightarrow FXe\bullet$$

$$FXe\bullet + F_2 \longrightarrow XeF_2 + F\bullet$$
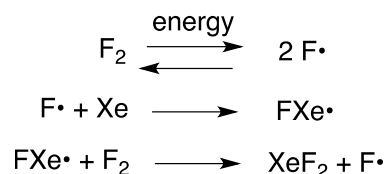
In this model, application of the steady-state approximation (in F•) predicts that the rate of formation of XeF_2 will be proportional to Xe pressure, so Yost and Kaye, using around 1/8 or 1/10 the Xe pressures of Hoppe or Streng and Streng, should have generated product at a rate around 8-10 times slower. In fact, that is almost certainly an overly *generous* estimate: mechanistic studies indicate that at higher Xe pressures reactions involving two Xe's start to become important (27):

$$Xe + F\bullet + Xe \longrightarrow FXe\bullet + Xe$$

$$2\ FXe\bullet \longrightarrow XeF_2 + Xe$$
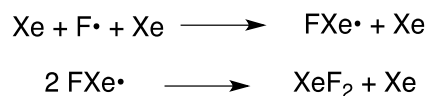
That implies a dependence on Xe pressure that should be *greater* than first-order, and hence Yost and Kaye should have produced XeF_2 more than an order of magnitude more slowly (everything else being equal) than did Hoppe or Streng and Streng. Hoppe saw significant product after a few hours; Streng and Streng, on the second day (of course, using exposure to sunlight they could only operate during daytime). Hence Yost and Kaye would have needed to run for at least a day, probably much longer, to see much of anything. Did they? They only mention "varying intervals of time," but it seems unlikely they would have carried on for multiple days.

It is probable that they *did* generate traces of product: the attack on the quartz observed was most likely the result of HF generated by hydrolysis of a very small amount of xenon fluoride. Their experimental procedures should have been good enough to exclude all but a *small* amount of adventitious water; if they *had* kept on for long enough, they might well have scrubbed all the water out of the system and started making observable quantities of product—which their methodology should indeed have permitted them to see.

We have seen that none of the interpretations previously proposed for Yost and Kaye's lack of success are consistent with the record, and that it does not seem fair to call anything they did do a mistake. They certainly *could* have chosen a gas mixture composition that would have been more likely to yield success—it is not at all clear why they did not—but with little or no mechanistic understanding (and how could they have had any, for an as yet unknown reaction?) there would have had no obvious reason to use higher Xe pressures. (Pauling also says, in his third letter to Allen, that he believes "there was plenty of xenon present" (7).) Alternatively, they *could* have carried out the experiment for much longer periods of time—probably days on end would have been needed—but their failure to do so, with nothing (good) visibly happening, is understandable.

It appears that relatively minor adjustments to some experimental details could well have yielded success, but they had no reason to believe the reaction should be so sensitive to their choices. We have to conclude that Yost and Kaye were just unlucky not to have opened up the field of noble gas chemistry, several decades ahead of the actual event.

References and Notes

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22. Pauling to J. C. Slater, Feb. 9, 1931. Courtesy AH & LPP.

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25. Hoppe's paper has a received date of October 8, 1962; the actual work had been done in late July 1962, according to his later commentary (1). Matheson's received date is November 5, 1962.

26. R. Hoppe, W. Dähne, H. Mattauch and K. Rödder, "Fluorination of Xenon," *Angew. Chem. Int. Ed.*, **1962**, *1*, 599.

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Chemical Heritage Foundation Launches *Distillations* Magazine

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ROBERT PERCY BARNES:
FROM HARVARD TO HOWARD UNIVERSITY

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Born in Shiloh, Maryland, on February 26, 1898, Robert Percy Barnes was the first African American to earn a Ph.D. in chemistry from Harvard University (Cambridge, MA) (1). As professor and head of the chemistry department at Howard University, he mentored several African American chemistry students and was a prolific scientific researcher with approximately 40 papers in high-impact journals from 1934 through 1963.

Robert was the second oldest child of Mary Jane Thomas and Reverend William Humphrey Barnes. Robert had one older brother William, and two younger brothers, Clifford and Kenneth. Barnes earned his B.S. degree in 1921 from Amherst College located in Amherst, MA (1, 2, 3). After completing his undergraduate degree, he joined the faculty at Amherst becoming the first African American appointed to the faculty. In 1922, he accepted a faculty position at Howard University, an HBCU (Historically Black College or University) located in Washington, DC. In 1922, he married Ethel E. Hasbrook and the couple resided in Washington, DC. The couple later divorced. Barnes married his second wife, Florence Abram Barnes on November 28, 1933. They were married 48 years until her death in 1981.

While teaching at Howard University, Barnes obtained a Fellowship (1928-1931) from the General Education Board (GEB) (4) to continue his education. The GEB was a philanthropy founded by John D. Rockefeller. Barnes earned his M.S. and Ph.D. from Harvard University in 1931 and 1933, respectively. Barnes

earned his Ph.D. under the direction of well-respected organic chemist Professor Elmer P. Kohler (5). In 1934, Barnes and Kohler published a peer-reviewed article in the prestigious *Journal of American Chemical Society (JACS)* (6).

Interestingly, Kohler had also worked with eminent steroid chemist Percy L. Julian, who earned his Master of Arts degree in chemistry from Harvard University in 1923. Unlike Barnes, Julian could not pursue his Ph.D. at Harvard University due to institutional racism. Julian was denied a teaching assistantship he needed to finance his education. He was not allowed to teach white students. In fact, Julian left the country and earned his PhD from the University of Vienna in 1931 (1). Furthermore, Kohler had also mentored renowned organometallic chemist, Henry Gilman, who went on to become a professor at Iowa State University (Ames, IA) (7,8). Gilman earned his Ph.D. in 1918 from Harvard under the direction of Kohler. Gilman mentored several African American chemistry students at Iowa State including, Nathanial O. Calloway (Ph.D., 1933) and Samuel P. Massie (Ph.D., 1946). Massie would later become the first African American faculty member at the US Naval Academy (7). Calloway responded (9) to a letter from Gilman discussing the dismal statistics of African Americans earning doctoral degrees in science and mentions Kohler and Julian:

> At the time I graduated from Iowa State I am quite certain that no one [that is, no African American] had

earlier obtained any sort of Ph.D. degree west of the Mississippi. In the East the story would have been different, although there had been a few. In chemistry, for example, your old professor Kohler, as you know, turned down Percy Julian flatly telling him that there was no place for him in the field of chemistry.

It is interesting (and ironic) that Kohler told Julian there was no place for him in chemistry considering Kohler served as the adviser for Barnes a decade after Julian earned his M.A. degree from Harvard. Why did Kohler change his perspective? Did Kohler finally believe that African Americans had a place in chemistry? Did Gilman influence Kohler's changing perspective? Calloway and Barnes earned doctoral degrees in chemistry in the same year (1933) becoming the first African Americans from their institutions to reach this achievement.

During his tenure at Howard University, Barnes focused his research efforts on the chemistry of diketone molecules, which are often used as starting materials to prepare other important organic molecules. Diketones have many applications in the health and beauty industry (e.g., cosmetics) and as food additives.

Barnes mentored several African American chemistry graduate students including Lewis A. Gist Jr., Harold Delaney and George W. Reed. Gist earned his M.S. degree from Howard University in 1949 and co-authored a *JACS* paper with Barnes (10) in 1950. Gist later earned his doctoral degree with Gilman at Iowa State in 1956 (8). Delaney earned his M.S. (1943) and his Ph.D. (1958) from Howard University, becoming one of the first three students to earn doctorates in chemistry at Howard. The Howard University chemistry department first offered the M.S. degree in 1923, just one year prior to Barnes joining the faculty there. Howard was the first HBCU to offer the doctoral degree in chemistry.

Reed earned his M.S. degree from Howard University in 1944 and later earned his Ph.D. from the University of Chicago in 1952. Both Delaney (11) and Reed (12) published their research efforts with Barnes in *JACS*. Delaney also published a paper with Barnes (13) in the *Journal of Organic Chemistry* in 1943. Furthermore, Delaney (14) and Reed (15) worked on the Manhattan Project during World War II at University of Chicago's Metallurgical Laboratory. The Project led to the development of the atomic bomb, which ended the war.

Barnes also mentored African American women chemistry graduate students at Howard University. Barnes published an article in *JACS* with Leila S. Green

(16) in 1938 and published three articles in the journal with Gladys E. Pickney (17) in 1947, 1953, and 1954. This is very significant because the opportunities for African American women in the chemical sciences were very limited during this time period (18). Green earned her M.S. degree from Howard in 1937. Pickney also earned her M.S. from Howard in 1946 and was employed as a chemistry associate in the Department of Chemistry at Howard in the 1950s.

In 1950, President Harry Truman appointed the initial Board of the National Science Foundation (NSF), an independent federal agency newly established, "to develop and encourage the formation of national policy for the promotion of basic research and education in the sciences." (At the time, NSF had an operating budget of $225,000.) Barnes was selected as one of the 24 scientists (not just chemists) appointed to the Board (19) in 1950, holding the position for 8 years. Barnes was chair of the Department of Chemistry at Howard during the time he served on the board.

Barnes retired from Howard University in 1967. He mentored several African American chemistry students earning advanced degrees and was a prolific scientific researcher publishing in high-impact journals. Barnes is the first African American to earn a PhD in chemistry from Harvard University, and he had a stellar career before the landmarks of the modern Civil Rights Movement. His achievements in academia are truly remarkable given the limited resources available for his research efforts. He died of cardiopulmonary arrest on March 18, 1990 at his home (3) in Washington, DC at the age of 92.

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SCIENCE AND POLITICS: A CASE STUDY OF THE CROATIAN CHEMICAL JOURNAL

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Introduction

It is not unusual for a scientific journal to change its name. The *Journal of Inorganic and Nuclear Chemistry*, found in 1955, changed its title to *Polyhedron* in 1982, *Chemistry World* was first published in January 2004 to replace *Chemistry in Britain*, which ran from 1965, etc. However, it is very unusual that a chemical journal in less than three decades (1927-1955) has changed its name six times—nearly as many times as *Liebigs Annalen*, which was continuously published under seven titles, but in the period of 165 years (1832-1997). This journal is *Croatica Chemica Acta* (1-6), the leading chemical journal in Croatia.

Croatian Journal with a Serbian title

The journal was first published in 1927 as *Arhiv za hemiju i farmaciju* (*Archives for Chemistry and Pharmacy*), as the supplement to the pharmaceutical journal *Farmaceutski vjesnik* (7). Its founder and the first editor was Vladimir Njegovan (1884-1971), the professor of inorganic and analytical chemistry at the Higher Technical School in Zagreb (founded in 1919). Croatian by birth, born and living in the capital of Croatia, Zagreb, Njegovan insisted on the Serbian language in his journal. Even the title of the journal was Serbian (*hemiju* instead of *kemiju*), and he wrote editorials in Serbian, not Croatian. However, papers were published in all three official languages of *Kraljevina Srba, Hrvata i Slovenaca* (the Kingdom of Serbs, Croats and Slovenes), founded imme-

diately after the "Great War" (on December 1, 1918). The kingdom was ruled by the Serbian Karađorđević dynasty. On October 3, 1929, the new state changed its name to Yugoslavia, after King Aleksandar enforced his personal dictatorship. The new name implied that all the subjects of King Aleksandar belong to the same (Yugoslav) nation. Accordingly, the territory of Yugoslavia was divided into new administrative units (*banovina*) with virtually no reference to historical, i.e. national borders (8).

All the subjects of the Yugoslav king were "Yugoslavs," but Croats and Serbs had quite different perceptions of their new state, and even more of the nature of Yugoslav nationality. A similar political constellation was also reflected in the foundation of *Jugoslavensko hemijsko društvo* (the Yugoslav Chemical Society) in Zagreb, the publisher of *Arhiv*, which despite its "Yugoslav" name did not encompass all the chemists in Yugoslavia. The problem was that Serbian chemists already had their society, the Serbian Chemical Society (founded in 1897), which had changed its name on December 31, 1926, to *Hemisko društvo Kraljevine Jugoslavije* (Chemical Society of the Kingdom of Yugoslavia). Croatian chemists insisted on the fusion of the two "Yugoslav" chemical societies, but the Serbian chemists strongly opposed this (9), stating that "A Chemical Society has to be representative of all chemists in the state and accordingly has to have the name of the state, as was recommended by the Constitution and has to have its seat in the capital" (i.e. Belgrade). The problem had even been put to the IUPAC Commission, but nothing was solved (10).

The next editor-in-chief of the journal, elected in 1934, was Franjo Hanaman (1878-1941), professor of inorganic chemistry and technology at the Technical Faculty, known as the inventor of the commercially viable electric bulb with tungsten filament. In 1938 the journal changed its title to *Arhiv za hemiju i tehnologiju* (Archives for Chemistry and Technology), for an obvious reason—the journal hadn't yet published a single paper "from any specific pharmaceutical field" (11). However, nothing essentially was changed. *Arhiv* persisted to be the journal of a wide scope almost exclusively aimed at the members (less than 200) of the Yugoslav Chemical Society—it published mostly short extracts from foreign journals, professional papers and communications to its subscribers. Yet, in 1938 the suggestion that papers in "foreign languages" should also be published was accepted (12).

However, in the same year, 1938, the journal once more changed its title becoming *Arhiv za kemiju i tehnologiju*. The change of a single letter (**h**emiju into **k**emiju) reflected a great turn in Yugoslav internal politics. After the end of the dictatorship of King Aleksandar (who was assassinated in Marseilles, France, on October 9, 1934), an agreement between Croatian and Serbian politicians has been achieved, crowned by the establishment, in October 1939, of the new federal unit, *Banovina Hrvatska* (Figure 1) (13). These events enabled also the establishment of Croatian Chemical Society (*Hrvatsko kemijsko društvo*).

Figure 1. *Croatia's borders in Banovina Hrvatska (1939-1941) closely corresponded to its borders in the Yugoslav republic (1945-1991), which are in turn identical to the borders of the Republic of Croatia (established in 1991).*

New State—New Title

On April 6, 1941, Germany and its allies attacked Yugoslavia, which formally capitulated on April 17, after only 11 days of fighting. However, on April 10 the puppet state *Nezavisna država hrvatska*—NDH (the Independent State of Croatia) was proclaimed (Figure 2) (14). These turbulent events also had repercussions on Croatian chemists. The Croatian Chemical Society changed its name to *Hrvatsko kemijsko društvo* and the journal's title to *Kemijski vjestnik* (Chemical Herald) (15). However, only one issue of *Kemijski vjestnik* was published (assigned as XV/XVI, 1941-42), with the help of the new editor Mladen Deželić (1900-1989), honorary professor of physical chemistry at the Philosophical Faculty in Zagreb (Figure 3). He replaced Stanko Miholić (1891-1960), obviously for political not professional reasons, because after the war Miholić continued to be the editor of *Arhiv* (1945-1953).

Figure 2. *The Independent State of Croatia (Nezavisna Država Hrvatska—NDH) encompassed larger territory than any Croatian state; however it was a German/Italian protectorate during the WWII (1941-1945).*

KEMIJSKI
VJESTNIK
(ARHIV ZA KEMIJU I TEHNOLOGIJU)

GOD. XVII.

UREDIO:
PROF. DR. MLADEN DEŽELIĆ
UZ SURADNJU UREĐIVAČKOG ODBORA
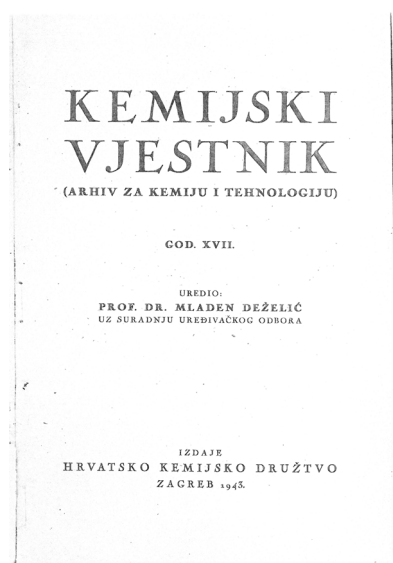
IZDAJE
HRVATSKO KEMIJSKO DRUŽTVO
ZAGREB 1943.

Figure 3. The journal name and its editor-in-chief lasted only one issue: the cover page of the Croatian chemical journal published during World War II.

Professor Deželić was a Croatian nationalist, who was not, because of his political views, permitted to do any responsible job in the Kingdom of Yugoslavia. However, the establishment of the NDH presented him with new opportunities. In 1942 he was quickly promoted to assistant professor and the first Head of the Department of Chemistry at the Zagreb Faculty of Pharmacy, founded the same year, and only after one year, in 1943, he advanced to the position of full professor at the same faculty. But at the end of the war, in 1945, he was expelled from the University and had to be satisfied with the job in controlling the quality of tobacco (16).

The same fate would have befallen Professor Hanaman, but in the NDH, if he had not already died. Namely, the last prewar issue of *Arhiv* was forbidden because of "too nice" an obituary to its late editor, whose "crime" was to be a Freemason. "If Professor Hanaman had been alive, he would surely be arrested, as happened to many of his colleagues at the University," said Professor Miholić at the first postwar session of the Croatian Chemical Society (17).

Croatian—but not too Croatian

The "new," communist Yugoslavia, which emerged in 1945 on the territory of the Kingdom of Yugoslavia, had a peculiar politics toward Croatian nationalism, as well as to nationalism of all major nations in the Yugoslav federation. It was essential to stop both Croatian separat-

ist and Serbian unitary extremists, known—according to names of their movements in World War II—as *Ustashe* (Croats) and *Chetnicks* (Serbs). It was, therefore, even politically incorrect to use the adjective *hrvatski* (Croatian) if it was possible to use the genitive expression *Hrvatske* (of Croatia) instead.

This "in between" politics was reflected in the name of the professional association of Croatian chemists, *Hrvatsko kemijsko društvo* (not *družtvo*!), HKD, and the name of their journal, *Arhiv za kemiju* (not *hemiju*!). Moreover, HKD was connected, as a member, to *Hrvatsko prirodoslovno društvo* (the Croatian Society for Natural Science), founded in 1885, and thus lost all formal ties with any possible "Yugoslav" chemical society (18).

After the war the journal restored its former name, but with deletion of *i tehnologiju* (and technology), obviously for pure professional reasons. However, about the next change of its title there was much ado.

The first glimpse came from the first editorial of the new editor. Božo Težak (1907-1980), professor of physical chemistry at the Zagreb Faculty of Science and the pioneer of information sciences in Croatia (19, 20), tried from the very beginning to promote the central Croatian chemical journal as an international periodical. It is noteworthy that he wrote his first editorial bilingually (Croatian and English) (1):

Today *ARHIV ZA KEMIJU* is almost exclusively a scientific periodical: as a rule, papers published in *ARHIV* are original contributions which have not been published elsewhere before. The papers are published either in Croatian with a summary in a foreign language, or in a foreign language with a summary in Croatian. Publication of scientific papers in Croatian (or any other of the Yugoslav languages) is allowed in order to develop our scientific terminology and to stimulate the work of our research schools.

And what about unitarity in chemistry? In this respect Professor Težak is clear (1):

Only under particularly favourable conditions where the views on science have become uniform, we may expect a superstructure such as *Acta Chemica Scandinavica*, published by the chemical societies of Scandinavia. We are endeavouring to achieve the same, though on a smaller scale, in our [federal] republic, by concentrating in *ARHIV* all scientific production in the field of chemistry.

The argument seems to be dubious. Why could Scandinavia, much more scientifically productive and far less politically coherent than Yugoslavia, have

its common chemical journal, and Yugoslavia couldn't? The problem was that the Serbian chemists had a similar journal, founded in 1930 as *Glasnik Hemiskog društva Kraljevine Jugoslavije* (Bulletin of the Chemical Society of the Kingdom of Yugoslavia; now *Journal of the Serbian Chemical Society*) and the chemists of both nations, Croatian and Serbian, were faced with a problem very similar to that of fusion of the two "Yugoslav" chemical societies.

The argument for the change of the name of the journal, presented at the Annual Plenary Meeting of the Croatian Chemical Society (February 16, 1955) was strictly technical (21). Professor Težak pointed out that the Swedish *Arkiv för Kemi* had nearly the same abbreviation, *Arkiv Kemi*, as the Croatian journal (*Arhiv Kem.*), and that might possibly make problems for the efforts to propagate the Croatian journal in foreign countries. He thus proposed the new title whose abbreviation cannot be confused with the abbreviation of any other journal: *Croatica Chemica Acta—Croat. Chem. Acta.* He also argued that other nations have journals with the similar names, e.g. *Helvetica Chimica Acta.*

"I want to say concerning this point that I recall the talk with Professor Težak, about a year ago, when we both were scandalized by the fact that we had changed the name of our journal five times," said Professor Hrvoje Iveković (1901-1991) at the meeting. "I think that 27 years in the life of a journal is quite enough time for its consolidation, at least concerning its name." Obviously, despite both professors being "scandalized," they took opposite positions. Professor Krešimir Balenović (1914-2003) contradicted Iveković: "Concerning the fact

Title of the Croatian Chemical Journal　　　**Political Status of Croatia**

Province of the Kingdom of Serbs, Croats and Slovenes (1918-1929)

1925

Arhiv za hemiju i farmaciju (1927-1938)

Arhiv za hemiju i tehnologiju (1938)
Arhiv za kemiju i tehnologiju (1938-1941)

Kemijski vjestnik (1941-1945)

1950

Arhiv za kemiju (1946-1956)

Historic province in the Kingdom of Yugoslavia (1929-1939)
Federal unit (*banovina*) of the Kingdom of Yugoslavia (1939-1941)
The Independent State of Croatia (German/Italian protectorate, 1941-1945)

Federal unit (republic) of Communist-ruled Federal Democratic Republic of Yugoslavia (1945-1963)

Constitutional reform increased autonomy of federal units (1953)

Croatica Chemica Acta (1956-)

1975

Federal unit (republic) of Communist-ruled Socialist Federal Republic of Yugoslavia (1963-1991)

2000

Republic of Croatia (1991-) (independent state)

Member of the European Union (2013-)

Figure 4. Timeline of the Croatian Chemical Journal.

that the journal has changed its title six times so far, I cannot see nothing tragic in it. In these 30 years the political system in Yugoslavia was changed, and many other things were changed, so it is not at all surprising that the names of our journal were also changed" (21).

But what about with the word *Croatica* (Croatian) in the proposed name of the journal? If the journal were proclaimed as Croatian, "it seems to me that it would discourage the people from Slovenia, Bosnia and Herzegovina, and other federal republics to publish in this journal," said Iveković, obviously the major opponent of the proposal. "This question has now political implications which—as it seems to me—nobody expected," said Dina Keglević (1922-2012), asking "Comrade Rector," i.e., Professor Iveković, who was apparently a member of the Communist Party, if the name "*Croatica*" were legal at all. It is legal, of course, answered "Comrade Rector," but "I have only pointed to the possibility that some not fully informed members could be for the change of title *also because* [his emphasis], i.e., because of such a title." In short, the word *Croatica* is not illegal, but it might cause political problems (21).

After the poll, 60% of altogether 458 members of the Croatian Chemical Society agreed to change the name of the journal, to a name—as Professor Težak said in the first editorial of the new (old) journal—that suggests the articles would be published in world languages (because of the Latin title) and indicates the closer territorial and national relation (22).

So ended the saga of the name of the Croatian chemical journal showing that in the history of chemistry political factors could be sometimes more influential than the purely professional ones.

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7. However, *Arhiv* was not the first Croatian chemical journal. In 1921 Svetozar Varićak (1894-1932), assistant professor at the *Gospodarsko-šumarki fakultet* (Faculty for Agronomy and Forestry) in Zagreb founded *Udruženje jugoslavenskih kemičara* (the Society of Yugoslav Chemists), which published *Revue Chimique*. The journal lasted only one year; 16 issues were published with 200 pages in all. In 1925 Njegovan reformed the society as *Jugoslavensko kemijsko društvo* (K. Balenović, "Lavoslav Ružička: Stara domovina i kemija u Hrvatskoj 1918-1988" ("Lavoslav Ružička: His Home Country and Chemistry in Croatia 1918-1988)," *Rad Jugoslav. Akad. Znan. Umjet., Kem.*, **1989**, *[443]7*, 131-198; V. Njegovan, "Iz redakcije" ("From the Editorial Board"), *Arhiv Hem. Farm.*, **1927**, *1*, 48).

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15. The new Croatian spelling must be noted (*družtvo* instead of *društvo*, and *vjestnik* for *vjesnik*). Croatian orthography was, and still is, strictly phonetic. The new nationalistic regime introduced etymological orthography to make the Croatian language as different as possible from Serbian (in which phonetic orthography is also in use). The change of *Arhiv* into *Vjestnik* should also be attributed to the new linguistic politics which preferred genuine Croatian words.

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EARLY HISTORY OF POLYPYRROLE: THE FIRST CONDUCTING ORGANIC POLYMER

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Introduction

Conjugated organic polymers (Figure 1) have grown to receive considerable academic and technological interest due to their combination of the electronic and optical properties of traditional inorganic semiconductors with many of the desirable properties of organic plastics, including mechanical flexibility and low production costs (1,2). In general, this class of polymers can be characterized as semiconducting materials that exhibit enhanced electronic conductivity (quasimetallic in some cases) in either their oxidized (p-doped) or reduced (n-doped) state (1,2). The resulting study of these materials has led to the current field of organic electronics, with considerable effort focused on the development of technological applications such as organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), field effect transistors (FETs), sensors, and electrochromic devices (1-4). In addition, the flexible, plastic nature of the conjugated organic materials used in these electronic devices has led to the realistic promise of flexible electronics in the near future (3,4).

Figure 1. *Common conjugated organic polymers.*

Discussions of the history of this field generally begin in the mid-to-late 1970s with the collaborative work of Hideki Shirakawa, Alan G. MacDiarmid, and Alan J. Heeger on conducting polyacetylene (5-8). In 2000, these investigators were awarded the Nobel Prize in Chemistry for their early contributions to the field of conjugated organic polymers. The language of the award further reinforces the common view of the historical origins of these materials which states that the award is "*for the discovery and development of electrically conductive polymers*" (9). It is only somewhat recently that reports have begun to present a more complete account of the early history of these materials, with particular attention given to highlighting the work that predates the commonly cited polyacetylene work of the 1970s (10-13). While this previous work may not have been as dramatic or as fully realized as the later polyacetylene studies, many aspects and relationships attributed to the work recognized by the Nobel prize can be seen in these earlier contributions.

Within this body of earlier work, the first real successful production of an organic polymer with significant conductivity was reported in 1963 by Donald Weiss and coworkers in Australia on conducting polypyrrole (14-16). In contrast, the modern polypyrrole literature

typically points to the later work of Diaz and coworkers in 1979 (17) in presenting the early studies of the material (18-20), which further supports the view that the history of conducting polymers begins with polyacetylene and that other members of the family of conjugated polymers followed afterwards. Of course, the history of polypyrrole does not even really begin with the work of Weiss and dates even further back to 1915 with work on a black precipitate named "*pyrrole black*" by Angelo Angeli (21-28). This current report will attempt to present a more complete and detailed account of the early history of polypyrrole up through the commonly referenced work of Diaz and coworkers.

Angeli and Pyrrole Black

Angelo Angeli (Figure 2) was born August 20, 1864, in the town of Tarcento, located in the Udine province of
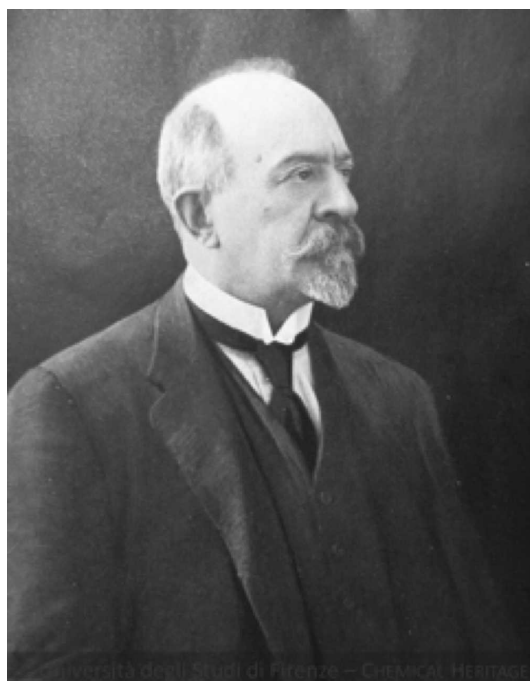
Figure 2. *Angelo Angeli (1864-1931). Courtesy of the "Ugo Schiff" Chemistry Department, University of Florence, Italy.*

northeastern Italy (29-31). The son of a modest merchant, he was forced to abandon his studies at the Technical School in Cividale del Friuli in order to help with the family business (29). His early passion for chemistry, however, was maintained by his close relationship with his uncles Giuseppe and Giovanni Carnelutti, who kept a small laboratory in their home and allowed him to participate in chemical experiments (29,30). At the

insistence of his mother (29), he ultimately returned to his studies, attending the Technical Institute of Udine (29-31). Following military service, he then enrolled at the University of Padua (29-31).

At Padua, Angeli began studying under the young Giacomo Ciamician (1857-1922), the new chair of general chemistry (29). Ciamician recognized his potential and asked Angeli to follow him to the University of Bologna in 1889 as his private assistant. Angeli then completed his studies at Bologna in 1891 (29-31), after which he obtained the *libera docenza* in 1893 (29,31). His growing body of published works permitted him to finish first in an academic competition for the chair in analytical chemistry in 1895 (29-31). Unfortunately, however, the competition was canceled without filling the chair (29,31).

While at Bologna, Angeli had also come to know Adolf von Baeyer (1835-1917). It has been said that von Baeyer recognized in Angeli a sure promise for Italian science and encouraged him to continue in his research (29-31). When Angeli won the chair of pharmaceutical chemistry at the University of Palermo in 1897 (29,31), he was initially unsure whether to accept the position (29). It was ultimately von Baeyer that persuaded him to accept the chair at Palermo (31) and Angeli then moved there in 1899 (29).

Angeli was called to Florence in 1905 to take up a vacant chair of chemistry at the Istituto di Studi Superiori (32), resulting from the death of Augusto Piccini (1854-1905) (29,30). He was reluctant to leave Palermo, but the poor health of his parents induced him to move back closer to family (29). He was asked to move to Rome in 1909 (29), but declined and remained at Florence where he took the chair of organic chemistry in 1916, a position specifically created for him by the University (30,31). In 1922, he was called back to Bologna to replace his former teacher, Giacomo Ciamician, but again he declined to leave the University of Florence and remained there until his death (29-31). He died from a fatal attack of pulmonary edema on Sunday, May 31, 1931, in his bedroom of a modest hotel where he had lived since his arrival in Florence in 1905 (30).

Angeli has been characterized as shy and introverted (29-31), finding it difficult to speak in public and limiting his participation in conferences or international meetings (30). Due to his nature, he never sought honors and awards. Still, his contributions were recognized, including being awarded the Military Cross for special services performed during World War I (31). In addition,

Angeli was repeatedly a candidate for the Nobel Prize in Chemistry from 1911 to his death (30).

As part of more general studies on the chemistry of pyrrole and indole, Angeli began studying the treatment of pyrrole with hydrogen peroxide/acetic acid mixtures as early as 1915 (22). Exposure of the heterocycle to these oxidizing conditions resulted in the formation of a black precipitate that he named "*nero di pirrolo*" or "*pyrrole black*" (21-23). Typically, one gram of pyrrole was dissolved in a sufficient amount of acetic acid, after which 2-3 grams of 50% H_2O_2 was added. After a short time, the solution became greenish brown, and over the space of a couple of days turned to black-brown. The product could be isolated as a thin black powder, either via spontaneous precipitation, dilution of the final solution with water, or addition of aqueous sodium sulfate (22,23). The product was insoluble in everything but basic solutions and purification methods included dissolution in base, followed by reprecipitation with either acetic acid or dilute sulfuric acid. The purified material was then filtered and dried at 120°C to give a fine powder of dark brown-to-black color (22,23).

Angeli went on to find that pyrrole blacks could be obtained using a variety of oxidizing agents (21), including nitrous acid (24), potassium dichromate (25) or chromic acid (27), lead oxide (25), oxygen and light (26), ethylmagnesium iodide and oxygen (26), potassium permanganate (26), and various quinones (27,28). Comparison of the results obtained from the different oxidants led Angeli to conclude (25):

> Questi fatti presentano uno speciale interesse perchè dimostrano che la formazione dei neri di pirrolo molto probabilmente è preceduta da un processo di polimerizzazione della molecola del pirrolo, che si compie in modo più o meno rapido a seconda dei reattivi che si impiegano.

> [These facts are of special interest because it shows that the formation of pyrrole blacks is most likely preceded by a process of polymerization of the pyrrole molecule, which takes place more or less rapidly depending on the reagents that are used.]

The isolated pyrrole black greatly resembled the natural pigment family of melanins (33) and chemical analysis revealed that pyrrole black contained N:H:C ratios similar to that of melanin (22,23). Further attempts to probe the structure of pyrrole black were limited by its insoluble nature, but included oxidative degradation to give cleavage products consistent with pyrrole and indole derivatives (22,23,25,26), leading to the conclusion that the pyrrole ring was retained in the structure of pyrrole

black. To further the scope of his study, Angeli found that the treatment of various functionalized pyrrole derivatives with oxidants could produce colored species, but did not result in the production of pyrrole black (24,25). Ultimately, his studies led Angeli to propose that the structure of pyrrole black contained units consisting of direct carbon-carbon bonds between pyrroles as shown in Figure 3a (25). It should be noted that this proposed structure is very similar to the currently accepted structure for oxidized portions of the polypyrrole backbone (Figure 3b).
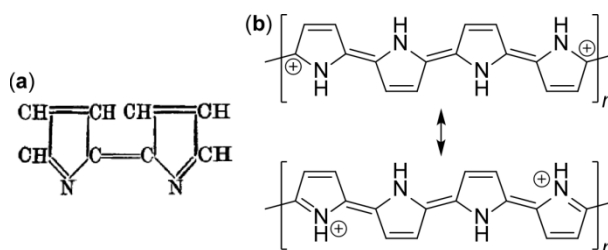

Figure 3. *(a) Angeli's proposed basic unit for the structure of pyrrole black (reproduced from Ref. 25); (b) modern resonance structures describing oxidized polypyrrole.*

Angeli ultimately concluded his work with pyrrole black in the early 1920s in order to move onto other research topics, although he did return to the subject with one final paper in 1930. At about that same time, however, another student of Ciamician, Riccardo Ciusa, began an independent investigation involving the polymerization of heterocycles in efforts to generate graphitic analogues from pyrrole, thiophene, and furan (34-36).

Ciusa and "Graphite" from Pyrrole

Riccardo Ciusa was born April 27, 1877, in Sassari, on the Italian island of Sardinia (37-39). He attended the Sassari Technical School before beginning studies at the University of Bologna in 1896 (37). In 1899, he then obtained a grant to attend the University of Torino, where he graduated *dottore* in chimica in 1902 (37,38).

After graduation, he returned to Sassari to become assistant of mineralogy for Prof. Boeris at the University of Sassari (37). In 1904, he obtained funding for specialized training abroad and traveled to Strasbourg to work in the laboratory of Prof. Johannes Thiele (37,38). He was then recommended to Prof. Ciamician by Prof. Gaetano Minunni of the University of Sassari, resulting in Ciusa's move to Bologna in 1906 (37).

After a brief time as assistant of agricultural chemistry, Ciusa became an assistant at the Istituto di Chimica

Generale in 1907, under the direction of Ciamician. The following year, he obtained the *libera docenza* in general chemistry, after which Ciusa taught the course on analytical chemistry at Bologna. He also went on to teach the chemistry of dyes and coloring at the newly founded Regia Scuola Superiore di Chimica Industriale di Bologna (37).

During World War I, Ciusa served as an infantry officer in the Italian Army. Upon his return to Bologna, he was named *aiuto* in 1919, a promotion granted to a limited number of the best assistants which included a small increase in salary (37,38). He then continued as assistant to Ciamician until the professor's death in 1922. After Angeli declined to return to fill Ciamician's position, Ciusa was appointed provisional director of the Istituto di Chimica Generale and was charged with taking over the teaching of general chemistry (37).

Ciusa was appointed professor of pharmaceutical chemistry at the University of Cagliari in November of 1922, but he elected to stay at Bologna instead. Then, in November 1924, he was appointed professor of pharmaceutical chemistry for the newly established University of Bari, where he remained until his retirement in 1960 (37-39). His research at Bari focused on pyrrole and its derivatives, including natural pyrrole-based species such as chlorophyll. He later became interested in plant chemistry and photochemistry, and served as Dean of Faculty from 1932-1952 (40).

At the end of his time as Ciamician's assistant, Ciusa began investigating the thermal polymerization of tetraiodopyrrole as a potential route to a material that could be considered a type of graphite generated from pyrrole (34-36). By heating tetraiodopyrrole in vacuum at 150-200°C, he produced a black material with a graphitic appearance. Analysis of this material gave an elemental composition corresponding to $[C_4NHI]_n$ (Figure 4), which Ciusa considered to be an intermediate in the formation of graphite (34-36). He later proposed the two structures given in Figure 5 as possible representations of this intermediate (36).
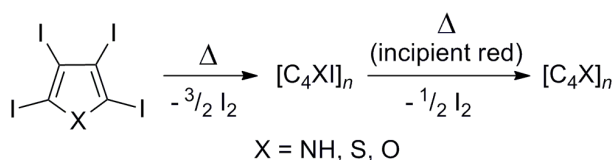
Figure 4. Thermal polymerization of tetraiodoheterocycles
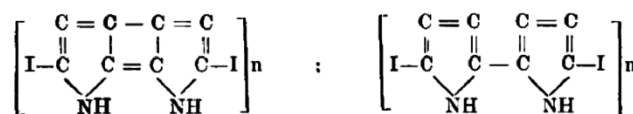
Figure 5. *Ciusa's proposed structures for $[C_4NHI]_n$ (reproduced from Ref. 36).*

Reheating this material at higher temperature (incipient red) liberated the final iodine atom to give a black material with similar appearance to graphite flakes and an elemental composition of $[C_4NH]_n$ (35). Ciusa went on to repeat this process with both thiophene and furan (Figure 3) to get similar results (35,36). He summarized the results of these efforts as follows (35):

> È notevole il fatto che nei tre casi studiati sinora, tre atomi di iodio si eliminano a temperatura relativamente bassa e contemporaneamente, mentre il quarto atomo si elimina in una fase successiva della reazione ed a temperatura più elevata.
>
> [It is remarkable that in the three cases studied so far, three atoms of iodine are eliminated at relatively low temperature and at the same time, while the fourth atom is eliminated in a later stage of the reaction and at a higher temperature.]

Finally, he applied this approach to the thermal polymerization of hexaiodobenzene to produce a graphitic material that he described as similar to ordinary graphite. Measurement of the resistivity of the synthesized material showed the low resistivity expected of graphite, although it was approximately six times more resistive than an authentic sample of graphite (37).

Unfortunately, Ciusa did not attempt to measure the resistivity of the heterocyclic graphites. In addition, he never reported any further characterization of these materials other than their graphite-like appearances and elemental compositions. It is also interesting to note that he never seemed to make any connection between the materials he was producing and the previous reports of pyrrole black by Angeli. Ciusa's work, however, did not go completely unnoticed. Nearly 40 years later, his thermal polymerization studies became the foundation of efforts by Donald Weiss and coworkers to produce conductive organic polymers (14-16).

Weiss and Conducting Polypyrrole

Donald Eric Weiss (Figure 6) was born October 4, 1924 (11,41-44) in the Melbourne suburb of St. Kilda, in Victoria, Australia (11,41,43). He was the only child of H. Vernon Weiss and Lillian née Le Lievre (11,41, 43), who separated when he was only 3 years old (41). Weiss

and his mother then moved to Adelaide (41), where he attended Mitcham Primary School and Scotch College (11,41-43,45). In 1942, he enrolled in the Industrial Chemistry degree program at the South Australia School of Mines (now part of the University of South Australia) (11,41-43). During his first two years, he did most of the courses at the adjacent University of Adelaide, finally transferring there in 1944 (41,43,45). In his third year, he failed Electrical Engineering I and had to repeat it by correspondence from Burnie, Tasmania (41), where he had found employment as a shift chemist for APPM (Australian Pulp and Paper Manufacturers) (41-46). He was ultimately awarded his BSc in 1945 (11,41,42,44).

Wanting to be involved in research, Weiss took a position in 1947 as a development chemist at Commonwealth Serum Laboratories (CSL, Melbourne), where he attempted to improve their new penicillin process (11,41-45). Early in 1947, he attended a meeting of the Royal Australian Chemical Institute (41) where he met Dick Thomas, who was the leader of the Minerals Utilization Section of the CSIR (Council for Scientific and Industrial Research) Division of Industrial Chemistry at Fishermen's Bend (another Melbourne suburb) (11,41,43,45). As a result, Weiss moved to CSIR (now CSIRO) on January 2, 1948 (41,42), to work under Dirk Zeidler in the Chemical Engineering Section, Division of Industrial Chemistry (11,41-45). In October of 1958, Weiss submitted a collection of his CSIR research to the University of Adelaide in support of his candidature for the degree of Doctor of Science (D.Sc.) (11,47). He was awarded the D.Sc. in 1960 (11,41,42,44).

Figure 6. *Donald E. Weiss (1924-2008)*, courtesy of Robert Weiss.

About this same time, Weiss began research on semiconducting organic polymers as potential electrically-activated and easily regenerated adsorbents for a proposed electrical process for water desalination (11,48). These efforts began in 1959 with the preparation of xanthene polymers (48,49). While these organic materials exhibited p-type semiconductor behavior, the measured resistivity was still quite high (R_{min} = 7-20 × 10^3 Ω cm) (49).

Weiss then came across the papers of Ciusa (34-36), which suggested that Ciusa's pyrrole "graphite" might provide a new approach for their efforts (11,48). As Ciusa had not reported the electrical properties of his pyrrole materials, Weiss and coworkers set out to reproduce the production of the previously reported pyrrole materials in order to characterize the resulting structure and potential conductivity. Weiss did not follow the exact methods of Ciusa (34-36), but used modified conditions in which a series of polymers was prepared by heating tetraiodopyrrole at temperatures as low as 120°C in a rotating flask under a flow of nitrogen. The nitrogen was used to both maintain an inert atmosphere and to transfer iodine vapor away from the reaction (14). The products of these reactions were reported to be insoluble, black powders, which were described as "polypyrroles" consisting of (14):

> ...a three-dimensional network of pyrrole rings cross-linked in a nonplanar fashion by direct carbon to carbon bonds.

Analysis of the products revealed that the determined composition did not agree with those reported by Ciusa and considerable amounts of oxygen were also found. It must be noted that Ciusa prepared his material in vacuum, while Weiss prepared his material under a nitrogen flow, which could at least partially account for the differences. Weiss, however, concluded that the oxygen arose from the adsorption of water and oxygen during the isolation and grinding of the product. This was then at least partially verified by finding that the oxygen could be driven off with heat, with the polymer then reabsorbing oxygen upon standing (14). In addition, it was found that the materials contained both "*adsorbed molecular iodine*" and nonreactive iodine which was concluded to be "*iodine of substitution*" (11,14). Based on the various descriptions given by Weiss and coworkers, a hypothetical structure for the polymeric material is given in Figure 7.
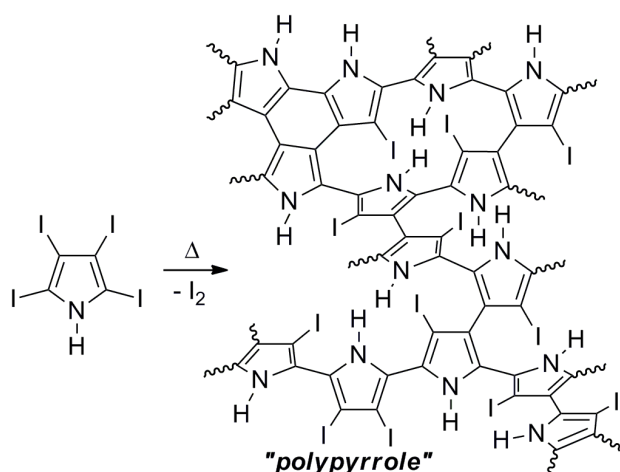
Figure 7. Hypothetical structure of Weiss's polypyrrole.

Electronic characterization of the polypyrrole powders were then carried out by measuring the resistivity (*R*) of pressed pellets under a stream of nitrogen to give values of 11-200 Ω cm at 25°C (16,50). In addition, a temperature-dependent study of the resistivity provided a temperature profile consistent with a standard semiconductor (16). These values correspond to conductivities (1/*R*) of 0.005-0.09 Ω^{-1} cm^{-1} and while they are still below that of carbon black, they are drastically better than the previous xanthene polymers and represented the highest reported conductivities for a non-pyrolyzed organic polymer. Weiss described the nature of this conductivity as follows (16):

> However it is apparent that the polymers are relatively good conductors of electricity. Since no polarization was observed during the measurement of the electrical resistance, even over substantial periods of time, it is assumed that the conductivity is of electronic origin.

Of significant interest was the discovery that the removal of adsorbed molecular iodine by either solvent extraction (16), chemical or electrochemical reduction (14,15), or thermal vacuum treatment (16) resulted in a significant increase in resistance. Electron spin resonance (ESR) studies then provided evidence for the formation of a strong charge-transfer complex between the polymer and iodine (15). This led to the following conclusion (16):

> Charge-transfer complexes of strength sufficient to cause partial ionization induce extrinsic [semiconductor] behaviour by changing the ratio of the number of electrons to the number of holes.

Thus, they understood that (14):

> The presence of the oxidant iodine, and in its absence oxygen, facilitates oxidation of the polymer.

Of course, this oxidative process (Figure 8) describes what would later be called p-doping of the polymer, which was ultimately determined to be the key to produce highly conductive organic polymers (1,6-9,13). Weiss, however, admitted that the full role of the iodine oxidation to conductivity was not realized at the time (48).
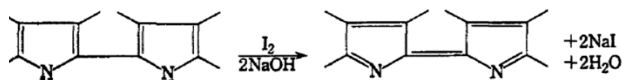

Figure 8. Iodine oxidation of polypyrrole under basic conditions (reproduced from Ref. 15 with permission of CSIRO Publishing).

Weiss and coworkers went on to study a few more related polymers (51-53), but ultimately determined that the use of these organic polymers for an electrical desalination process was impractical and thus moved on to other projects by 1967 (11,48). In February 1974, he became the Chief of CSIRO's newly formed Division of Chemical Technology (41) and it was during these years that he made his most well-known contributions. Most notable of these were the development of magnetic ion-exchange resins and SIROFLOC, a large-scale continuous water treatment process (43,45,48). During his career, Weiss earned a number of prestigious awards, including his being made an Officer (OBE) of the Most Excellent Order of the British Empire in 1976 for his contribution to science (11,42,43). After 36 years at CSIRO, Weiss retired in October of 1984 (11,41-43,48). He then passed away on July 30, 2008, in the eastern suburb of Blackburn (41) due to pneumonia brought on by a battle with lung cancer (43,54).

Pyrrole Black at the University of Parma

About the time that Weiss and coworkers were wrapping up their work with the polypyrrole-iodine materials, resurgence in the study of pyrrole black was occurring in Italy at the University of Parma. This was primarily due to the research of Luigi Chierici (d. 1967), Gian Piero Gardini (d. 2001), and Vittorio Bocchi (55-61). While the specifics of their collaborations are not clear, it appears that Chierici was the guiding force behind these efforts as he was already studying pyrrole black as early as 1953, before either of the others had come to Parma. Of the three, it is Gardini of whom we have the most knowledge. After receiving a degree in Industrial Chemistry from the University of Bologna in 1961, he moved to the University of Parma in 1962 and joined Chierici as a professor in the Institute of Pharmaceutical

Chemistry (62). The final member, Bocchi, then joined them about 1966. The three did not work together for long, however, as Chierici died on March 3, 1967 (58,61), leaving Gardini and Bocchi to carry the research forward.

Parma founded the Institute of Organic Chemistry in 1968, which included both Gardini and Bocchi as faculty. Within this new organizational structure, both men worked under the Director of the Institute, Prof. Giuseppe Casnati (63). Gardini was then appointed to the chair of organic chemistry in 1980 (62,64). In 1984, he succeeded Prof. Casnati as Director of the Institute, which then became the Department of Organic and Industrial Chemistry in 1992, with Gardini remaining as Director (62,63). He continued as Director of the Department until 1998 (62,63), before dying in 2001 (64).

These efforts were a fairly direct extension of the previous work of Angeli. Most of their efforts focused on identifying the intermediates and byproducts formed during the oxidative polymerization of pyrrole with H_2O_2 (55-58), with Gardini concluding in 1973 that the mechanism needed much more research to be well defined (18). However, the most significant results came via collaboration with Parma's Institute of Physics, which focused on ESR studies of pyrrole black (59,60). The first of these studies utilized pyrrole blacks produced via Angeli's initial H_2O_2/acetic acid conditions (59). In the second study, however, the polymeric material was obtained via electrolysis (60), thus representing the first example of an electropolymerized polypyrrole (18,19). The polymer was obtained by applying a constant current of 100 mA to a platinum electrode in a solution of pyrrole in H_2SO_4. Over a period of two hours, a laminar film formed on the electrode, which was then rinsed with distilled water and dried under vacuum (60). X-ray analysis of the film indicated that the material was essentially amorphous and conductivity measurements gave a room temperature value of 7.54 Ω^{-1} cm^{-1}, considerably higher than that reported by Weiss and coworkers for the thermally-produced polypyrrole-iodine materials (16). It should be pointed out that these results were not compared to the previous work of Weiss and coworkers, nor is there any evidence that the Parma researchers were even aware of previous reports of conducting polypyrrole materials. Lastly, the ESR studies indicated the presence of antiferromagnetic interactions, strongly interacting polymer chains, and highly mobile electrons, although the spin density was found to not be very high (60).

In an additional study, Chierici and Bocchi then analyzed the electropolymerized material via oxidative degradation (61). While additional degradation products of unknown composition were detected in comparison to the traditional pyrrole blacks produced via H_2O_2 oxidation, the major product for all materials was pyrrole-2,5-dicarboxylic acid. This led to the conclusion that all of the pyrrole blacks studied consisted of chains of α,α'-linked pyrroles (Figure 1) (61).

In 1975, Gardini spent time as a visiting scientist at the IBM Research Laboratory in San Jose, California (62). This initial visit was repeated with additional stays in 1978 and 1981 (62). It was during these visits that Gardini began working with Arthur Diaz.

Diaz and Electropolymerized Polypyrrole Films

Arthur F. Diaz was born in 1938 in southern California (65). After high school, he attended San Diego State University, receiving a B.S. in Chemistry in 1960 (66,67). He then pursued graduate studies at UCLA under Dr. Saul Winstein (1912-1969), earning his Ph.D. in 1965 (65-67). He stayed on at UCLA, first as a post-doctoral researcher and then a research associate, before eventually being hired by TRW Systems (66). He then joined the Department of Chemistry at the University of California, San Diego, as an Assistant Professor in 1969 (66,67). In 1974, he spent one year as a Program Officer for the Educational Division of the National Science Foundation, before returning to California to join the IBM Almaden Research Laboratory in San Jose, where he became manager of the Advanced Materials group (66,67). After 20 years at IBM, he retired in 1995 and joined the Department of Chemical and Materials Engineering at San Jose State University (66,67).

Upon arriving at IBM, Diaz was charged with developing a new project of significant impact, preferably in the area of electrochemistry, as IBM was interested in building capabilities in this area (66). This led to an interest in modifying the surfaces of electrodes, resulting in some time studying monolayers and thin films. Conducting polymers were becoming a current hot topic, and he considered the use of such materials for modified electrodes, but was unsure as to how to make this work with polyacetylene (66). It was at this point, during one of Gardini's visits to IBM, that Gardini mentioned to Diaz about the pyrrole black work being done at Parma, particularly the most recent success in electropolymerization (66).

The combination of the material's intractability and conductivity intrigued Diaz and thus he began investi-

gating the generation of electropolymerized films (66). After a matter of time, Diaz was able to perform the electropolymerization of pyrrole under controlled conditions, allowing the generation of strongly adhered films onto electrode surfaces in a reasonable and repeatable manner (17,66). Diaz found that the use of deoxygenated aprotic solvents resulted in better material properties (17,68) than the previous aqueous conditions utilized in the Parma work (60). Under optimum conditions, the polypyrrole films were synthesized galvanostatically on a platinum surface from pyrrole in a 99:1 acetonitrile-water mixture with tetraethylammonium tetrafluoroborate as a supporting electrolyte (17,19,68). It was found that the water content of the solution could be used to control the adherence of the film to the substrate. Absence of water produced poorly adhering, non-uniform films, while adherence improved with increasing amounts of water (68).

Elemental analysis of the material indicated that it was primarily coupled pyrrole units, plus BF_4^- anions, in the ratio of ca. 4:1 (17,68). It was concluded that the pyrrole units of the polymer backbone carried a partial positive charge balanced by the BF_4^- ions (69,70). The pyrrole-linked structure was confirmed by Raman and reflective IR analysis showing bands characteristic of pyrroles (69). Consistent with the previous Parma study, electron diffraction indicated that the films were not very crystalline, showing only diffuse rings corresponding to a lattice spacing of 3.4 Å (69).

The electrical conductivity of thicker free-standing films (5-50 mm) were examined via four-point probe to give room temperature conductivities of 10-100 Ω^{-1} cm^{-1} (17,18,68-70). Diaz thought that the drastically improved conductivity in comparison to the Parma results was at least partially due to higher quality films resulting from the fact that he grew his films slowly and very thin (70). In comparison, his impression was that the Parma films were quite thick (66). It is now fairly well understood that the structural order of the film decreases with the corresponding film thickness, which also results in a decrease in film conductivity. As with the previous materials reported by Weiss and coworkers (16), temperature-dependent conductivity measurements of the electropolymerized films revealed a temperature profile consistent with a classical semiconductor (69,70).

Conclusions

The above discussion has hopefully illustrated the extensive work reported on polypyrrole dating back to the earliest work of Angeli in 1915, nearly 65 years before the seminal work of Diaz in 1979. While most of these reports used the earlier term of *pyrrole black* to refer to these materials, it is quite clear from their discussions and analysis that these materials in question were polypyrrole. In addition, the electrically conductive nature of this material has been known since the work of Weiss and coworkers in 1963, with the magnitude of its conductivity significantly increasing with each sequential improvement in the polymer's production. It is also important to note that with the exception of the work of Diaz, all of the research presented above occurred before the collaborative polyacetylene work of Heeger, MacDiarmid, and Shirakawa (10-13). As such, it is hard to support the statement quoted in the introduction that these three gentlemen discovered electrically conductive polymers, although their early contributions definitely sparked the broad interest in the field.

It should also be pointed out that the work of Diaz and coworkers discussed herein has significance beyond the simple fact that it represented the highest conductivity of polypyrrole in the early years of the growing field of conjugated organic polymers. While he was not the very first to report the electropolymerization of a conjugated polymer, Diaz was the one that not only optimized this process in terms of quality and reproducibility, but then demonstrated that this could be broadened to a wide family of conjugated systems. As a result, electropolymerization quickly became the most common method for the generation of conjugated polymeric films, until it was ultimately supplanted by the current focus on soluble, processible materials.

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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. Peterson. As a postdoctoral associate, he then studied conjugated organic polymers under Prof. James E. Hutchison 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 application of history to chemical education, the history of materials and chemical technology in antiquity. Prof. Rasmussen currently serves as the Program Chair for the ACS History of Chemistry division and as Series Editor for *Springer Briefs in Molecular Science: History of Chemistry*, as well as holding editorial positions for the journals *Fluorescent Materials* and *Topological and Supramolecular Polymer Science*.

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BOOK REVIEWS

The Lost Elements: The Periodic Table's Shadow Side, Marco Fontani, Mariagrazia Costa, and Mary Virginia Orna, Oxford University Press, New York, 2014, 576 pp, ISBN 978-0-19-938334-4, $39.95

It is easy to fall into the trap of presenting the history of chemistry as nothing but a succession of successes as the frontiers of knowledge move triumphantly from one new discovery to another. Chemical historians recognize that this is untrue, but there is rarely time, even in a multi-credit historical survey course, to focus on the false pathways and mistaken ideas that bedeviled scientific progress. This book provides a welcome antidote to this oversight by focusing on the history of new elements that were incorrectly proposed to be added to the periodic table, what these authors call lost elements. The authors estimate (see page 417) that over 200 incorrect claims of new elements have been proposed, so the false claims actually outnumber the elements known today.

The book is divided into seven sections, which present the various spurious claims of new elements in roughly historical order. The first section deals with the period from 1750 to 1789, that is, prior to the development of the modern definition of an element. This is the shortest section of the book due to a combination of the limited number of individuals doing chemical research at the time and the lack of sophisticated methods of analysis. Perhaps the most interesting historical figure considered in this section is Christian Friedrich Samuel Hahnemann (1755-1843). In 1801, Hahnemann announced that he had discovered a new alkali metal that would expand up to twenty times in volume upon heating. He named the new element *pneum-alkali*, since its behavior seemed to resemble that of the lung. When his proposal was ridiculed to extinction, Hahnemann turned his attention to medicine, where he espoused the theory of homeopathy, that is, the medicine should be chosen based on the similarity

of its effect to the symptoms of the disease to be treated. This approach was not well received either, although the idea continues to attract followers even today.

The second section, 1789-1869, deals with the period between Lavoisier's definition of a chemical element and the formulation of the periodic table of the elements by Dmitri Mendeleev. One of this reviewer's favorite chapters in this section identifies new elements that were proposed with so little confidence that the "discoverers" didn't even bother to propose a name. The authors of *Lost Elements* call these ghost elements. Part of the attraction may be due to surprise that someone who was proposing a new element would lack enough commitment to even suggest a name, but also it is interesting that the scientists who fall into this category include Charles Frederick Chandler, one of the founders of the American Chemical Society and a former President of the Society, as well as Friedrich Genth, who also served as President of the ACS. Obviously even the most reputable of chemists can make these kinds of mistakes.

The third section, 1869 to 1913, focuses on the time between Mendeleev's creation of the periodic table and Moseley's recognition of the importance of atomic number. Although more powerful techniques, like spectroscopy and chromatography, became available for elemental separation and identification, isolation of the elements continued to be very challenging. Many of the lanthanides were so difficult to separate that there were frequent cases were mixtures of these elements were announced as being pure samples of new elements. Hafnium represented another difficult situation. It was the next to last of the nonradioactive elements to be identified, and before this happened there were more false claims to have isolated it than any other element in the periodic table. Also during this time period Sir William Ramsay had the distinction of being the only scientist

to have discovered or contributed to the discovery of an entire periodic group, the noble gases or Group 0 on the modern periodic table. Even as careful a scientist as Ramsay was not perfect; he was forced to admit that he had erroneously identified the presence of an inert gas in the atmosphere which he called *metaargon*.

In the fifth section, covering from 1939 to the present, most of the new elements beyond uranium are discovered either by physicists or by the chemistry group led by Glenn T. Seaborg. Searching for transuranium elements was a very expensive process, and the main competition to find the missing pieces of the periodic puzzle developed between teams in Dubna, Russia, and Berkeley, California, USA. From the beginning of the process there were incorrect reports of new elements. Enrico Fermi and his team claimed to have discovered several transuranium elements, but it was recognized later that they had actually created nuclear fission. Some scientists claimed to have discovered evidence for superheavy elements in meteorite fragments, and one researcher even claimed that heavy elements were involved in the metabolism of fish and other invertebrates. In another case, the claim of a new element was outright fraud, something that is surprisingly rare in the stories of this book.

One might expect that the general acceptance of periodicity would result in fewer false claims of new elements. After all, as the periodic table was filled in there were fewer empty positions where a new element might be placed. This is not the case, as described in section six, which discusses what the authors call "bizarre elements" that have no place in the periodic table. Various scientists proposed the existence of new elements lighter than hydrogen that were basic building blocks of matter. Some of these false elements came in both male and female forms. Even Mendeleev fell into this trap by not only proposing that the imponderable fluid, *ether*, was an element lighter than hydrogen but also by extrapolating its atomic weight. Perhaps most bizarre of all, a small group of clairvoyants announced that they could "see" the microscopic world of atoms and molecules, which certainly would be a helpful skill if it actually existed.

They proposed a new element, with the suggestive name, *occultum*, and eventually claimed to have detected 59 new elements by means of their special talent.

The chapters in section seven of the book do not deal as much with incorrect claims of new elements as they do with spurious reports of elemental transmutations, that is, modern alchemy. Radioactive decay as well as transmutation by subatomic particle bombardment are well known, but the transmutations described in this section were supposed to have occurred by other means, including even biological action. Various scientists reported transmutations of mercury into gold, silver into gold, lead into mercury, hydrogen into helium and neon, and dozens of other elemental transformations in biological systems. The book also includes a brief description of the reports of room temperature (i.e. "cold") fusion reactions.

The authors summarize by writing that the main lesson to be learned from the history of false claims of new elements is that individual scientists are not always right, but the scientific process continually moves towards a more accurate understanding of nature. Some scientists publically retract their mistakes (although they may hide their retraction by writing it in Latin and in an obscure journal), and unfortunately some obstinately refuse to admit that they were wrong. Obviously, the process is not as clear and straightforward as one might desire, but it is valuable to understand that true science must be based on theories that can survive testing by the scientific community.

Overall, this book gives a fascinating insight into an aspect of science that is sometimes overlooked, the recognition and correction of scientific error. The book is by no means light reading for the non-scientist, but historians of chemistry should enjoy reading about both the careers of many lesser known chemists as well as finding some familiar characters caught in rather embarrassing situations.

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Great Minds: Reflections of 111 Top Scientists, Balazs Hargittai, Magdolna Hargittai, and Istvan Hargittai, Oxford University Press, New York, 2014, 416 pp, 978-0-19-933617-3, $34.95.

Great Minds is a collection of excerpts from conversations the authors had with 111 scientists in the late twentieth century; the complete transcripts of these conversations can be found in *Candid Science*, a six-volume work published from 2000 to 2006 (London: Imperial College Press). *Great Minds* is divided into three sections, each of which focuses on individuals who worked within a specific discipline—physics, chemistry, or biomedical science—and there are roughly equal numbers of excerpts within each section. The authors readily admit that in many instances, a scientist situated within the physics section, for example, could also have been placed within the one that focuses on biomedical science quite justifiably; these disciplinary distinctions were not meant to constrain perceptions of scientific work but simply to serve as a general principle for organization. A brief biography and a photograph of the scientist precede each excerpt, and, on average, each excerpt is two pages in length. The content of the extracted conversation varies greatly, so greatly, in fact, that any themes that emerge—such as mentorship, science and the public, and gender and scientific practice—are purely coincidental, another detail to which Hargittais allude in their preface.

What the book is missing, though, is any discussion of context: why certain questions were asked during the conversations and others not, why these specific passages were of interest to the authors, and why, other than being "top scientists" (which in itself was not defined, though one can assume it is because over two-thirds of the scientists were Nobel laureates and many of the others worked with Nobel laureates), anyone should care about what these people said in their conversations. Take, for example, the excerpts from Mildred Cohn and Roald Hoffmann: Cohn worked with a number of Nobel laureates throughout the course of her career, and so the selection the Hargittais chose focuses on Cohn's reflections about Harold Urey; Hoffmann grew up in Europe during the Second World War, and the Hargittais decided to emphasize his schooling and learning foreign languages while avoiding Nazis. But the reader is given no understanding of what made these specific passages of such great interest to the authors. Stories told are not just about what is said, but *why* they are being said, especially within a broader conversation. Having read these passages, a reader is able to learn a bit about Urey and about education available to Jews in hiding in Nazi-

occupied countries during the Second World War, but a greater understanding of the relevance of the excerpts in a broader context and of the individuals themselves is much harder to know since the interviewees' words were extracted from conversation, from context.

I have not read any part of *Candid Science*, but I am quite familiar with the oral history of Mildred Cohn that the Center for Oral History at the Chemical Heritage Foundation conducted and I am in the process of interviewing Hoffmann so as to include his oral history within that same collection. Comparing the content of those oral history interviews to the excerpts that the Hargattais provide raises a number of questions. For example, did the Hargittais ask about Cohn's work with Nobel laureates and other scientists only or did they ask Cohn about being a female scientist in a male-dominated career? Did the topic of the sexism she experienced in her first job after completing her degree come up in conversation? Were Hoffmann's experiences of the war different from other Jews avoiding the Nazis? Did these experiences, in some way, affect the way he undertook the scientific enterprise? What about his work in the humanities? Did he talk about that at all or was the conversation solely about his childhood experiences in war-torn Europe? Distilling interviews down into short pieces for consumption without discussing intent—the interviewer's or the interviewee's intent—or creating a purposeful organizational structure diminishes what can be learned from speaking with and to others about their experiences, beliefs, thoughts, and practices. The Hargattais do not convey what made these specific selections more interesting than other content from the conversations, and, as such, make them into abstractions instead of situations for learning.

The power of interviews does not come from individuality but from collectivized knowledge: it is easy to dismiss what one person says as unique but much harder to do so when multiple voices are all saying similar or the same things. I fully admit that many of the passages in *Great Minds* are interesting as vignettes about the lives of these scientists, but I finished the book not knowing why the authors wanted me to care about any of these men and women or what I was supposed to learn from them. Again, the authors did mention that they noticed themes emerging in their selections, even pointing out several for the reader, but you need more than a couple of pages extracted from an interview in order to fully appreciate a person's relevance and learn about the significance of what he or she said—elucidation helps create meaning that can lead to understanding.

It is without a doubt that many of the 111 scientists whose extracts make up this book would be known to other scientists, but there are a number whose relevance to the scientific enterprise may not be as well known. The Hargattais tell us in their preface that there were different motives for why *they* wanted to interview these men and women, but they go no further, blinding the reader to an understanding of the historical value of the interviewees and what they had to say. Outside of the scientific community, the names of a few of these people may resonate from a memory of a chemistry class, but mostly they will not, making the utility of such a text quite limited to the general public. I fully believe that scientists have very important things to say, not just about science, but about politics, religion, culture, and the arts, for example, which is why I interview them for a living. Explaining to others why what scientists say matters is not self-evident: it needs to be contextualized and communicated. The Hargattais, regrettably, did neither in an effective way.

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