

Review

# Before Radicals Were Free—The *Radical Particulier* of de Morveau

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**Abstract:** Today, we universally understand radicals to be chemical species with an unpaired electron. It was not always so, and this article traces the evolution of the term radical and in this journey, monitors the development of some of the great theories of organic chemistry.

**Keywords:** radicals; history of chemistry; theory of types; valence; free radicals

## 1. Introduction

The understanding of chemistry is characterized by a precision in language such that a single word or phrase can evoke an entire back-story of understanding and comprehension. When we use the term “transition element”, the listener is drawn into an entire world of memes [1] ranging from the periodic table, colour, synthesis, spectroscopy and magnetism to theory and computational chemistry. Key to this subliminal linking of the word or phrase to the broader context is a defined precision of terminology and a commonality of meaning. This is particularly important in science and chemistry, where the precision of meaning is usually prescribed (or, maybe, proscribed) by international bodies such as the International Union of Pure and Applied Chemistry [2]. Nevertheless, words and concepts can change with time and to understand the language of our discipline is to learn more about the discipline itself. The etymology of chemistry is a complex and rewarding subject which is discussed eloquently and in detail elsewhere [3–5]. One word which has had its meaning refined and modified to an extent that its original intent has been almost lost is *radical*, the topic of this special issue.

This article has two origins: firstly and most importantly, on the occasion of his 80<sup>th</sup> birthday, it is an opportunity to express our gratitude and thanks for the friendship and assistance of Bernd Giese in our years together in Basel, and secondly to acknowledge a shared interest with Bernd in the history of our chosen discipline.

## 2. Modern Understanding

It seems relevant to present the IUPAC definition of a radical in full at this point in the text as it both provides a precision for modern usage and also contains hints of the historical meaning:

“A molecular entity such as  $\cdot\text{CH}_3$ ,  $\cdot\text{SnH}_3$ ,  $\text{Cl}\cdot$  possessing an unpaired electron. (In these formulae the dot, symbolizing the unpaired electron, should be placed so as to indicate the atom of highest spin density, if this is possible.) Paramagnetic metal ions are not normally regarded as radicals. However, in the ‘isolobal analogy’, the similarity between certain paramagnetic metal ions and radicals becomes apparent. At least in the context of physical organic chemistry, it seems desirable to cease using the adjective ‘free’ in the general name of this type of chemical species and molecular entity, so that the term ‘free radical’ may in future be restricted to those radicals which do not form parts of radical pairs. Depending upon the core atom that possesses the unpaired electron, the

radicals can be described as carbon-, oxygen-, nitrogen-, metal-centered radicals. If the unpaired electron occupies an orbital having considerable s or more or less pure p character, the respective radicals are termed  $\sigma$ - or  $\pi$ -radicals. In the past, the term 'radical' was used to designate a substituent group bound to a molecular entity, as opposed to 'free radical', which nowadays is simply called radical. The bound entities may be called groups or substituents, but should no longer be called radicals" [6].

To summarize, in accepted modern usage, a radical possesses an unpaired electron.

### 3. A Radical Birth

#### 3.1. de Morveau's Introduction

The word radical was introduced by the French politician and chemist, Louis-Bernard Guyton, Baron de Morveau (1737–1816, prudently identified after the French revolution without the aristocratic rank as Louis-Bernard Guyton-Morveau, Figure 1) [7]. In 1782, de Morveau published an article entitled *Sur les Dénominations Chymiques, La nécessité d'en perfectionner le système, et les règles pour y parvenir* in which he identified the need for a new systematic nomenclature in chemistry [8]. In this paper, he not only formulated his five principles of nomenclature which later became embodied in the *Méthode de Nomenclature Chimique* [9,10], but also introduced the word *radical* to describe a multiatomic entity; in his own words "Having found the adjectives arsenical and acetic consecrated by usage, it was necessary to preserve them and form only such close nouns to the radicals of these terms that they could be understood without explanation. Arseniates and acetates seemed to me to fulfil this condition." He makes no further comment on the term in this paper, which also includes a table which lists acids, the generic names of salts derived from these acids, bases or substances that bind to acids. This table also confirms that he was still a phlogistonist [11,12] in 1782, as phlogiston is listed amongst the bases or substances that bind to acids. The word *radical* itself seems to derive from the Latin word *radix* (root).



**Figure 1.** Louis-Bernard Guyton, Baron de Morveau (1737–1816, subsequently Louis-Bernard Guyton-Morveau) was a French chemist and politician who introduced the word radical in 1782. (Public domain image. Source [https://en.wikipedia.org/wiki/Louis-Bernard\\_Guyton\\_de\\_Morveau#/media/File:Louis-Bernard\\_Guyton\\_de\\_Morveau.jpg](https://en.wikipedia.org/wiki/Louis-Bernard_Guyton_de_Morveau#/media/File:Louis-Bernard_Guyton_de_Morveau.jpg)).

By the time of the publication of the *Méthode*, the concept of radicals was embedded in the core of the model in five classes of substances which had not been decomposed into simpler materials (the second class includes all the acidifiable bases or radical principles of the acids) [9,10]. In this work, the "radical of the acid" was precisely defined as "the expression of acidifiable base". The explanations given in the text are difficult for the modern reader to follow as the conversion of the

radical (such as nitrate or acetate) to the parent acid did not involve the addition of protons but rather oxygen. Although the credit for the discovery of oxygen should be shared between William Scheele, Joseph Priestley and Antoine Laurent de Lavoisier [13,14], Lavoisier's contribution included the name *oxygène*, from the Greek ὀξύς (acid, sharp) and -γενής (producer, begetter), on the basis of his belief that oxygen was a constituent of all acids. On this basis, the *Méthode* continues to clarify the nomenclature of radicals defining known acids as arising from the addition of oxygen to "pure charcoal, carbon or carbonic radical... Sulphur or sulphuric radical ... and phosphorus or phosphoric radical". The identification of oxygen as the essential component of an acid was not without its difficulties and for elements such as sulfur, with variable oxidation states, it was necessary to state that "it is evident that the sulphur is at the same time sulphuric radical, and sulphureous radical". Additional problems arose with nitrogen derivatives, with de Morveau using both *Azote* and *Radical Nitrique* for the parent radical. It took Jean Antoine Chaptal [15] to introduce the name *nitrogène* in his 1790 work *Eléments de chimie* [16,17].

The text of the *Méthode* uses the term radical extensively to describe acids and their salts and the construction of the names is illustrated in the extensive tables correlating the old names with the ones which are newly proposed. One of the most important features of the *Méthode* was the folding table of substances in which the core radicals are identified.

One aspect of the establishment of the concept of radicals is reminiscent of the later work of Mendeleev, who proposed missing elements from the periodic table and identified their likely properties. In the same way, the *Méthode* recognizes that muriatic acid (modern name hydrochloric acid) contained an unknown radical, described as muriatic radical or muriatic radical principle. The extension of the radical concept to organic chemistry was also pre-empted by de Morveau when he noted that the reaction of sucrose with nitric acid to give ethanedioic acid (*acide saccharin*), which is a combination of oxygen and *radical saccharin*.

### 3.2. Lavoisier's Adoption

The use of the term radical in the original sense of de Morveau was broadly adopted by Antoine-Laurent de Lavoisier and his wife Marie-Anne Pierrette Paulze Lavoisier [18–21] in a number of subsequent and influential texts (Figure 2). The *Méthode* was republished and expanded [22], but the most influential was the *Traité Élémentaire de Chimie, Présenté dans un Ordre Nouveau, et d'Après des Découvertes Modernes* [23–25]. This also served to further bring the changes in nomenclature and philosophy to the attention of the anglophone world, which received the first translation of the *Méthode* in 1788 and was able to delight in the English translation of the *Traité* from 1791 onwards [22,26–29,30]. The radical concept is intrinsic to the book and is also clearly defined "The word acid, being used as a generic term, each acid falls to be distinguished in language, as in nature, by the name of its base or radical. Thus, we give the generic names of acids to the products of the combustion or oxygenation of phosphorus, of sulphur, and of charcoal; and these products are respectively named, phosphoric acid, sulphuric acid, and carbonic acid". In his list of elements in the *Traité*, Lavoisier lists *Radical muriatique*, *Radical fluorique* and *Radical boracique* (the elements chlorine, fluorine and boron respectively) as unknown (*Inconnu*). In the context of organic chemistry, Lavoisier recognized that organic compounds contained compound radicals which could combine with oxygen to form more complex substances, such as ethanol or ethanoic acid. We are fortunate that not only was Marie-Anne Pierrette Paulze Lavoisier an enthusiastic and gifted co-worker (and according to the *mores* of the times, not listed as a co-author), but that she also actively contributed to the *Traité* and preserved many of Antoine Lavoisier's writings, including his notebooks, for the benefit of future generations.



**Figure 2.** Antoine-Laurent de Lavoisier (1743–1794, subsequently Antoine Lavoisier) popularized the use of the term radical (Public domain image. Source [https://commons.wikimedia.org/wiki/File:Antoine\\_Laurent\\_de\\_Lavoisier.png](https://commons.wikimedia.org/wiki/File:Antoine_Laurent_de_Lavoisier.png)).

#### 4. From *Radical Particulier* to the Radical Theory and the Theory of Types

##### 4.1. Gay-Lussac and the CN Radical

The next player in our drama of radicals should be Joseph Louis Gay-Lussac [31] (Figure 3a) and, in particular, his work on cyanides. Although HCN (hydrocyanic acid, prussic acid) was a known compound, Gay-Lussac established its formula and showed that it contained no oxygen, another of the nails in the coffin of Lavoisier's theory that all acids contained oxygen. By 1815, he had prepared metal cyanide salts as well as ClCN and cyanogen and correctly identified that the CN unit was retained throughout chemical transformations. His publication *Recherches sur l'acide prussique*, repeatedly refers to the *radical de l'acide prussique* [32–35]. This, in turn, necessitates a subsequent and consequent linguistic distinction between “simple radicals” (iron, sulphur, nitrogen, phosphorus and carbon) and “compound radicals”; containing multiple elements bonded together but which behave as distinct (and inseparable) units. As Gay-Lussac wrote “Here, then, is a very great analogy between prussic acid and muriatic and hydriodic acids. Like them, it contains half its volume of hydrogen; and, like them, it contains a radical which combines with the potassium, and forms a compound quite analogous to the chloride and iodide of potassium. The only difference is, that this radical is compound, while those of the chloride and iodide are simple” [36]. In isolating cyanogen, Gay-Lussac claimed to have isolated the first compound radical (actually the dimer, (CN)<sub>2</sub>).

The identification of compound radicals was further expanded by Jöns Jacob Berzelius in 1817. Berzelius (Figure 3b) was the leading exponent of the electrochemical dualism theory which considered that all compounds are salts derived from basic and acidic oxides [37,38]. As one of the most respected chemists of the time, Berzelius' support for this model resulted in its widespread acceptance. For example, Berzelius would regard the compound potassium sulfate, K<sub>2</sub>SO<sub>4</sub>, as arising from the combination of the positively charged metal oxide K<sub>2</sub>O and negatively charged SO<sub>3</sub>. The radical theory as applied to inorganic compounds meshed well with his views, but he had difficulties in extending these to organic species. Nevertheless, he considered that the new concept of simple and compound radicals would clarify the differences between the inorganic acids with simple radicals and the organic acids with compound radicals “In inorganic nature all oxidized bodies contain a simple radical, while all organic substances are oxides of compound radicals. The radicals of vegetable substances consist generally of carbon and hydrogen, and those of animal substances of carbon, hydrogen and nitrogen” [39]. In reality, Berzelius refused to accept the possibility that a

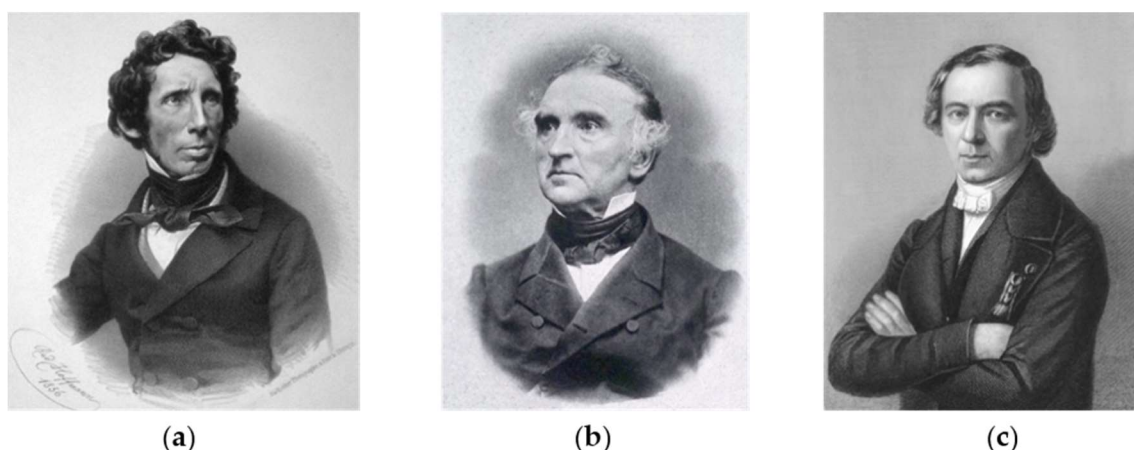
radical could contain oxygen and this, ultimately, led to the discrediting of the theory. In the intermediate period, however, the compound radical model was the origin of a new radical theory for organic chemistry and ultimately the modern functional group model.



**Figure 3.** (a) Joseph Louis Gay-Lussac (1778 – 1850) showed that CN was a compound radical and opened the doors to the Radical Theory of organic chemistry. (Public domain image. Source [https://en.wikipedia.org/wiki/Joseph\\_Louis\\_Gay-Lussac#/media/File:Gaylussac.jpg](https://en.wikipedia.org/wiki/Joseph_Louis_Gay-Lussac#/media/File:Gaylussac.jpg)) (b) Jöns Jacob Berzelius (1779 – 1848) was one of the leading chemists of his age and in 1817 he laid the basis for the Radical Theory in organic chemistry. (Public domain image. Source [https://en.wikipedia.org/wiki/Jöns\\_Jacob\\_Berzelius#/media/File:Jöns\\_Jacob\\_Berzelius.jpg](https://en.wikipedia.org/wiki/Jöns_Jacob_Berzelius#/media/File:Jöns_Jacob_Berzelius.jpg)).

#### 4.2. The General Radical Theory

The stage is now set for the generalization of the radical theory. The major players in this were Friedrich Wöhler (Figure 4a) [40], Justus Freiherr von Liebig (Figure 4b) [41,42] and (at least for a period) Jean Baptiste André Dumas (Figure 4c) [43]. The three had a vision of radicals as collections of atoms that behaved like elements and persisted through chemical reactions, although Dumas subsequently shifted his allegiance to the theory of types (Section 4.3).



**Figure 4.** (a) Friedrich Wöhler (1800–1882) showed that CN was a compound radical and opened the doors to the Radical Theory of organic chemistry. (Public domain image. Source [https://en.wikipedia.org/wiki/Friedrich\\_Wöhler#/media/File:Friedrich\\_Wöhler\\_Litho.jpg](https://en.wikipedia.org/wiki/Friedrich_Wöhler#/media/File:Friedrich_Wöhler_Litho.jpg)) (b) Justus Freiherr von Liebig (1803–1873) was one of the leading chemists of his age and in 1817 he laid the basis for the Radical Theory in organic chemistry. (Public domain image. Source [https://en.wikipedia.org/wiki/Justus\\_von\\_Liebig#/media/File:Justus\\_von\\_Liebig\\_NIH.jpg](https://en.wikipedia.org/wiki/Justus_von_Liebig#/media/File:Justus_von_Liebig_NIH.jpg)) (c) Jean Baptiste André Dumas (1800–1884).

One of the critical publications was *Untersuchungen über das Radikal der Benzoesäure* by Liebig and Wöhler in 1832 [44], which introduces synthetic chemistry in a manner that we rarely see today “If it is possible to find a bright point in the dark area of organic nature, which seems to us to be one of the entrances through which we can perhaps reach true paths of exploration and recognition ... From this point of view, one may consider the following attempts, which, as far as their extent and their connection with other phenomena is concerned, leave a wide, fertile field to cultivate”. In a way, this publication was somewhat heretical, at least in the eyes of Berzelius, as Wöhler and Liebig maintained that a radical could be more than just the base of an acid. Specifically, Wöhler and Liebig showed that the benzoyl radical ( $C_6H_5CO$  in modern formulation) persisted in the compounds  $C_6H_5CO-H$ ,  $C_6H_5CO-OH$ ,  $C_6H_5CO-Cl$ ,  $C_6H_5CO-I$ ,  $C_6H_5CO-NH_2$ ,  $C_6H_5CO-Br$ , and  $(C_6H_5CO)_2S$ . The conclusion was that the benzoyl radical behaved in a similar manner to an inorganic radical and persisted unchanged through multiple reactions.

The impact of this publication on the organic chemistry community cannot be underestimated and resulted in an explosive reporting of new radicals over the next few years, including acetyl, methyl, ethyl, cacodyl ( $Me_2As$ ), cinnamoyl ( $C_6H_5CH=CH$ ), and  $n-C_{16}H_{33}$ . Originally, Dumas was opposed to the radical theory but eventually became convinced by Liebig’s arguments. Dumas was responsible for the recognition of the methyl, cinnamoyl and  $n-C_{16}H_{33}$  radicals. Although the radical theory has not survived, the nomenclature introduced is still in use today. Berzelius himself was responsible for the identification of the ethyl radical [37,45]. The state-of-the-art in radical theory in the Berzelius spirit is found in another publication of Liebig which interprets a large number of experimental results on ethers in terms of the Berzelius radical model [46].

By 1837, although Dumas and Liebig still disagreed in detail on which groups of atoms were to be considered radicals, they were sufficiently confident in the universality of their radical model, that they published their “Note on the present state of organic chemistry”, which is a comprehensive overview of the radical theory at that time [47]. It appears that Liebig was given to flights of purple prose “and that, we are convinced, is the whole secret of organic chemistry. Thus, organic chemistry possesses its own elements which at one time play the role belonging to chlorine or to oxygen in mineral chemistry and at another time, on the contrary, play the role of metals. Cyanogen, amide, benzoyl, the radicals of ammonia, the fatty substances, the alcohols and analogous compounds—these are the true elements on which organic chemistry is founded and not at all the final elements, carbon, hydrogen, oxygen, and nitrogen elements which appear only when all trace of organic origin has disappeared. For us, mineral chemistry embraces all substances which result from the direct combination of the elements as such. Organic chemistry, on the contrary, should comprise all substances formed by compound bodies functioning as elements would function. In mineral chemistry, the radicals are simple; in organic chemistry, the radicals are compound; that is all the difference. One year later, in 1838, Liebig clearly defined what he understood by the term radical, in the context of the CN radical: “So we call cyanogen a radical, because 1) it is the non-changing constituent in a series of compounds, because 2) it can be replaced in them by other simple bodies, because 3) it can be found in its connections with a simple body of the latter, and represented by equivalents of other simple bodies. Of these three main conditions for the characteristic of a composite radical, at least two must always be fulfilled if we are to regard it in fact as a radical” [48].

The proposals of Liebig were not universally accepted. Robert Hare in the United States of America published a number of articles dismissing the commonality of the oxoacids and “simple” acids such as the hydrogen halides, well summarized in his monograph “An attempt to refute the reasoning of Liebig in favor of the salt radical theory” [49]. Berzelius, in particular, came to have difficulties with the radical theory of Wöhler and Liebig because it directly challenged his electrochemical dualism theory [50]. For example, the relationship between benzaldehyde  $C_6H_5CO-H$  and benzoyl chloride  $C_6H_5CO-Cl$  could not possibly be correct because the hydrogen which has a positive charge cannot be replaced by a negative chlorine.

Not only were ever more radicals being identified, but they were also being isolated as chemical species. A few highlights serve to exemplify this. Robert Wilhelm Bunsen (1811–1899) reinvestigated some arsenic compounds first reported by Cadet and obtained a foul-smelling and highly toxic liquid

which he called *Alkarsin*, although Berzelius suggested that cacodyl (or kakodyl) was more appropriate. The compound, formulated  $(\text{CH}_3)_2\text{As}$  [51] was obtained from the reaction of  $(\text{CH}_3)_2\text{AsCl}$  with zinc and was widely thought to be the free cacodyl radical. This compound was subsequently shown to be the dimer,  $(\text{CH}_3)_2\text{AsAs}(\text{CH}_3)_2$ . Similarly, Kolbe isolated the free methyl radical [52] and Frankland the free ethyl radical [53], although both were actually the dimers (ethane and butane, respectively).

#### 4.3. The Theory of Types

The theory of types is rather a difficult concept for the modern chemist to appreciate. Put simply, it retains the fundamentals of the radical theory, but allows the replacement of elements and groups within a radical. With hindsight, it is possible to see the origins of the functional group model of organic chemistry within this approach. The development leading to the theory of types came from Dumas, who in 1838 described the chlorination of acetic acid to give trichloroacetic acid [54–57]. The substitution of hydrogen by chlorine generated a new radical (trichloroacetyl or trichloromethyl rather than acetyl or methyl) but did not change the molecular *type*. The chemical properties of acetic acid and trichloroacetic acid were very similar, indicating the same molecular type. Dumas published two papers which enunciated his theory of types [55,56]. The level of vitriol and animosity in the debate is well exemplified by the spoof publication by S. C. H. Windler (actually written by Wöhler) in *Annalen* in which he rather wickedly parodies the substitution theories of Dumas and colleagues [58]. He describes sequentially replacing atoms in manganese(II) acetate (his formulation,  $\text{MnO} + \text{C}_4\text{H}_6\text{O}_3$ ) with chlorine, initially producing manganese(II) trichloroacetate and eventually,  $\text{Cl}_2\text{Cl}_2 + \text{Cl}_8\text{Cl}_6\text{Cl}_6$  (i.e.,  $\text{Cl}_{24}$ ). This compound was a yellow solid resembling the original manganese(II) acetate, because “hydrogen, manganese, and oxygen may be replaced by chlorine, there is nothing surprising in this substitution”. In a footnote, he adds “I have just learned that there is already in the London shops a cloth of chlorine thread, which is very much sought after and preferred above all others for night caps, underwear, etc.”

By 1853, primarily due to the work of Charles Adolphe Wurtz, Hoffman, Williamson and Gerhardt, four different types had been identified; the water type, the hydrogen type, the hydrogen chloride type and the ammonia type. The water type included water, alcohols, ethers and carboxylic acids, the hydrogen type, dihydrogen, and alkanes, the hydrogen chloride type included organohalogen compounds such as  $\text{C}_2\text{H}_5\text{Cl}$  and finally, the ammonia type which included all primary, secondary and tertiary amines [59].

#### 4.4. Laurent and the Theory of Types

Auguste Laurent (1807–1853) also studied substitution reactions and from 1834 onwards described numerous examples in which hydrogen atoms within radicals were replaced by halogens or oxygen [60–62]. Probably, the credit for the theory of types should be shared by Laurent with Dumas, because the former clearly recognized that the fundamental properties of the compound were not significantly changed by the substitution [63–65]. His theories are clearly stated in his book *Méthode de Chimie* from 1854 [66] but the ideas are clearly formulated (and seen to be almost identical to those of Dumas) as early as 1836 “All organic compounds are derived from a hydrocarbon, a fundamental radical, which often does not exist in its compounds but which may be represented by a derived radical containing the same number of equivalents” [67]. It appears that Dumas deliberately underplayed the importance of Laurent and over-emphasized the relevance of his protégé Henri Victor Regnault. On occasion, Laurent expressed his feelings in plain rather than scientific language “...others, pretend that I have taken some ideas of M. Dumas. ... M. Dumas has done much for the science; his part is sufficiently great that one should not snatch from me the fruit of my labors and present the offering to him” [68]. And concerning radicals, he wrote “I claim with a conviction most profound that to me belongs, and to me alone, the most part of the ideas developed by M. Dumas” [69]. The arguments continued!

In 1837, Laurent developed a theory of fundamental and derived radicals, subsequently known as his nucleus theory, which was based upon an obscure geometrical argument and attempted to

rationalize the carbon core of radicals undergoing substitution. Like much of his work, this was an interesting and novel attempt to bring order to organic chemistry [70]. Nevertheless, the theory of Laurent was anathema to Liebig, who in his usual offensive manner discussed it “not because he found something in it worthy of mention, not in order to admit its having an influence on the development of chemistry but in order to demonstrate that it is unscientific, good for nothing”.

#### 4.5. Dualities, Inconsistencies and Ambiguities within the Radical Theory

Even at the time of its greatest success, there were many inconsistencies and dualities within the radical theory. Today, we would understand the term acetyl radical to refer to the species  $\text{CH}_3\text{CO}$ . Unfortunately, this was not the case in the 19<sup>th</sup> Century CE. In 1835, Henri Victor Regnault (1810–1878) [71,72] reported a new radical  $\text{C}_2\text{H}_3$  (formulated  $\text{C}_4\text{H}_6$  at the time) which he termed *aldehydène* [73]. This radical was present in the compounds  $\text{H}_2\text{C}=\text{CHCl}$ ,  $\text{H}_2\text{C}=\text{CHBr}$ ,  $\text{BrCH}_2\text{CH}_2\text{Br}$  and many others that he isolated. He also linked the radical aldehydène to ethanal and ethanoic acid, which Regnault formulated as  $\{\text{C}_4\text{H}_6\text{O} + \text{H}_2\text{O}\}$  and  $\{\text{C}_4\text{H}_6\text{O}_3 + \text{H}_2\text{O}\}$ , respectively. In 1839, Liebig suggested that the radical  $\text{C}_2\text{H}_3$  should be called acetyl, in accord with his own system of nomenclature [74]. This 1839 paper of Liebig served to link together in a more-or-less coherent manner the various radicals and radical theories which had been proposed for  $\text{C}_2$  compounds (although with the atomic weight confusion at the time many of these were formulated  $\text{C}_4$  species). The Aetherin (or etherin) theory was proposed by Dumas and Boullay in 1828 and considered that  $\text{C}_2\text{H}_4$  (formulated  $\text{C}_4\text{H}_8$  at the time) was the common radical in  $\text{C}_2$  compounds: thus,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  and  $\text{C}_2\text{H}_5\text{Cl}$  were the aetherin radical with water, ethanol and HCl, respectively [75]. In contrast, Berzelius formulated these compounds in terms of the  $\text{C}_2\text{H}_5$  (ethyl) radical [37,45].

## 5. Valency Displaces Radicals

The real death of the old radical theory and the theory of types came in 1852 when Edward Frankland formulated what was to become the concept of valency, “When the formulae of inorganic chemical compounds are considered, even a superficial observer is struck with the general symmetry of their construction ... it is sufficiently evident ... no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms” [76]. Frankland’s combining power was the first formulation of the basic idea of valence and the entry to the electronic view that has dominated chemistry ever since.

A few years later, in 1858, Kekulé proposed a fixed valence for elements; although he did not equate the combining power with valence [77]. Kekulé successfully rationalized the structures of organic compounds by assuming a fixed valence of four for carbon, and extended this fixed valence idea to the elements nitrogen and oxygen which had fixed valences of three and two, respectively. The fixed valence of four for carbon necessitated multiple bonds (or free valences) in appropriate compounds. And so modern organic chemistry was born—or rather, as we have seen on a number of occasions in this article, we can testify to another of its births!

It is one of the pleasures associated with the study of the development of chemistry in the 19<sup>th</sup> Century CE, to read not only the contemporary primary literature, but also the textbooks and monographs of the period. These often provide a unique view of the way in which views changed and also give an understanding of the tensions and controversies in the science of the time. One of the lesser known works of this period is “A Short History of the Progress of Scientific Chemistry in Our Own Times” by William Tilden, which gives a detailed account of the evolution of chemistry to the last year of the 19<sup>th</sup> Century CE. The sections on the development of the Theory of Types and the subsequent Valency Model are excellent and also document a number of the poorly documented highways and by-ways associated with the scientific journey to the Valency Model [78]. An excellent contemporary (1867) overview of the Theory of Types and the relationship to the atomicity of the radicals is given by Adolphe Wurtz [79].

An interesting historical overview of the development of the subject written after the triumph of valency theory is to be found in the books by von Meyer [80] and Venable [81].



## 6. The Freeing of the Radical—the First Modern Radicals

Although transition metal compounds with unpaired electrons were well-known, and “simple” inorganic substances, such as Frémy’s salt ( $K_4[ON(SO_3)_2]_2$ ) [82], NO or NO<sub>2</sub>, which fulfill our modern definition of a radical had been long established, the dominance and success of the valence theory in organic chemistry, based upon the invariable and inviolable tetravalency of carbon led to the widely accepted opinion that organic radicals (modern sense) could not exist. The confidence in the tetravalency of carbon and the complacency of the organic community was shattered in 1900, when Moses Gomberg at the University of Michigan reported the preparation of triphenylmethyl radical, Ph<sub>3</sub>C·, as the product from the attempted preparation of hexaphenylethane from the reaction of chlorotriphenylmethane with zinc [83]. The title of the paper, “An instance of trivalent carbon: triphenylmethyl” hints at the supremacy of the “tetravalent carbon” dogma [84].

The rest, dear reader, is history.

## 7. Final Words

In this short article, we have presented a story which describes the evolution of organic chemistry and which laid the basis for our modern understanding based on the electronic, molecular orbital and functional group approaches. Perhaps surprising for the modern reader is the passion with which the debate was conducted and the manner in which the personalities of the individual involved come through and, indeed, the personalization of the rhetoric. The well-known *Schwindler* article has already been referred to. The correspondence between Berzelius, Liebig, Dumas and Wöhler is a wonderful introduction to the art and science of denigrating your rivals in language that is rarely found in the scientific literature [85]. The discourse was not limited to scientific matters, but also to the character and nationality of the players, for example, Liebig described Dumas on various occasions as a swindler, charlatan, tightrope dancer, Jesuit, highwayman, and a thief, like “nearly all Frenchmen” [86]. As he became older, Berzelius became increasingly cantankerous, and writes of Liebig “I will say nothing of Liebig’s ruthless, thoughtless and unjustified criticism, ... it just disappoints and saddens me... with the manner of a dictator, who wishes to abolish an old constitution and create a new one ... I hold it unlikely that he will take the slightest notice of my advice” [85]. Berzelius again, talking of Liebig “Either Liebig is mad, which I already began to painfully fear a year ago, in which case he deserves the pity of everyone and needs to be treated accordingly, or he is an unwise, inflated fool” [85]. Wentrup has recently published an assessment of some aspects of the debate in the context of Zeise’s discovery of his eponymous salt,  $K[Pt(C_2H_4)Cl_3]$  which also documents the acrimonious exchanges between the players [86].

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