Ask the Historian

Why is R Used for Hydrocarbon Substituents?

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Question

Why is R used to symbolize hydrocarbon substituents?

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Answer

The symbol R was first extensively used in the writing of generalized organic formulas by the French chemist, Charles Gerhardt (figure 1), in his famous *Précis de chimie organique* of 1844, a work which pioneered the use of generalized functional groups and homologous series to organize the known organic compounds of carbon (1). Gerhardt's choice of the letter R remains something of a mystery. The most obvious explanation is that was an abbreviation for the word "radical" - a term introduced by the French chemist, Guyton de Morveau, in 1786 to designate the element or combination of elements which formed acids upon reacting with oxygen (2). By the early 19th century, however, the term had come to stand for any reactive monoatomic (simple radical) or polyatomic (compound radical) fragment of a larger molecule that maintained its identity throughout a series of chemical reactions (3).

A second, less likely, candidate for R is the word "residue" and its German equivalent "Rest." These terms had been introduced by Gerhardt in 1839 as part of his famous residue theory of organic reactions. This postulated that such reactions were driven by the elimination of small, stable, inorganic molecules, such as H_2O, HCl, NH_3, etc., the accompanying organic by-products being merely the result of the haphazard combination of the left-over organic fragments or residues found in the starting molecules after extraction of the necessary components for the primary inorganic product (4).

Gerhardt's use of the letter R in his *Précis* is not completely consistent with either of these explanations, as he used it to symbolize both hydrocarbon molecules and the hydrocarbon portion of more complex molecules or, as he phrased it, to represent "les eléments combustibles." Indeed, he later restricted its use to

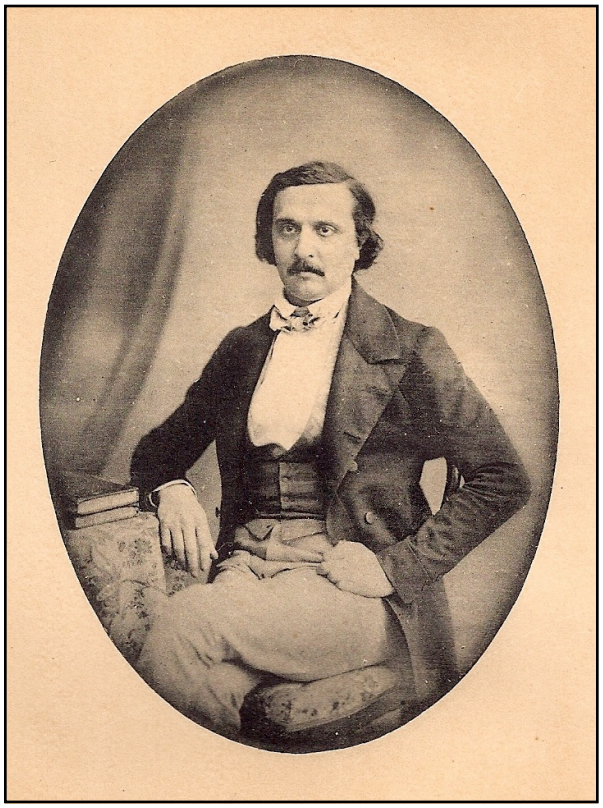

Figure 1. Charles Frédéric Gerhardt (1816-1856).

hydrocarbons and hydrocarbon fragments containing a 2/1 ratio of hydrogen to carbon (i.e. C_nH_{2n}) and employed more elaborate symbols to indicate other ratios, such as R+2 for C_nH_{2n+2} and R-4 for C_nH_{2n-4}, etc.

In his *Méthode de chimie*, of 1854, Gerhardt's friend and sometime collaborator, the French chemist, August Laurent, used R in Guyton de Morveau's original sense to generalize the formulas of various binary oxides (i.e., RO, RO_2, R_2O_3, etc.), as well as to symbolize the hydrocarbon nucleus or "noyau" of various organic molecules (5). This dual usage was carried over in Cannizzaro's famous pamphlet of 1858 on the determination of atomic weights, which contains the first explicit identification of R with the word radical that I am aware of (6):

I indicate by the symbol R^l_m *any monoatomic metallic*

radical, whether simple or compound, and with the symbol R^{II}_m any biatomic metallic radical.

By monatomic and biatomic, Cannizzaro meant monovalent and bivalent. In general, his simple radicals corresponded to electropositive atoms or elements and his compound radicals to hydrocarbon fragments. He also introduced the symbol X to represent electronegative substituents, such as O, OH, and the halides.

Following Cannizzaro, Mendeleev, in his famous review of 1871, made extensive use of R to represent generalized classes of atoms or elements when writing type formulas for both the oxides (R_2O, RO, RO_2, etc.) and hydrides (RH, RH_2, RH_3, etc) - formulas which were enthroned at the top of the short form of the periodic table for more than 70 years (7). In contrast, the early organic textbooks by Löwig (1846), Gregory (1852), Kolbe (1854), and Limpricht (1855) made no use of the symbol, though it does briefly appear in the 1867 text by Erlenmeyer, after which its use in the organic literature slowly increases throughout the rest of the 19th and early 20th centuries (8).

Literature Cited

1. C. Gerhardt, *Précis de chimie organique*, Vol. 1, Fortin et Masson: Paris, 1844, pp. 29-30, 36-46.
2. G. de Morveau, Ed., *Encyclopédie méthodique (chymie)*, Vol. 1, Panckoucke: Paris, 1786, p. 142. Morveau had in fact used R to symbolize radical in a table published the next year in the journal *Observations sur la physique*, **1787**, *30*, 81, but there is no evidence that this influenced Gerhardt.
3. J. B. Dumas, J. Liebig, "Note sur l´état actuel de la chimie organique," *Comptes rendus* **1837**, *5*, 567-572.
4. C. Gerhardt, "Sur la constitution des sels organique à acides complexes et sur leurs rapports avec des sels ammoniacaux," *Ann chim. phys.* **1839**, *72*, 181-214.
5. A. Laurent, *Méthode de chimie*, Mallet-Bachelier: Paris, 1854, pp. 177-189, 425-425.
6. S. Cannizzaro, "Sunto di un corso di filosofia chimica," *Il nuovo cimento* **1858**, *7*, 321-366. Translated as *Sketch of a Course of Chemical Philosophy*, Alembic Club Reprint No. 18, Livingstone: Edinburgh, 1949. Quote on page 41 of translation.
7. D. Mendeleev, "Die periodischen Gesetzmässigkeit der chemischen Elemente," *Ann. Chem. Pharm.* **1872**, *8 (Suppl.)*, 133-229. English translation available in W. B. Jensen, Ed., *Mendeleev on the Periodic Law: Selected Writings, 1869-1905*, Dover: Mineola, NY, 2005, pp. 38-109.
8. E. Erlenmeyer, *Lehrbuch der organischen Chemie*, Winter: Leipzig, 1867, pp. 186, 210.

Do you have a question about the historical origins of a symbol, name, concept or experimental procedure used in your teaching? Address them to Dr. William B. Jensen, Oesper Collections in the History of Chemistry, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172 or e-mail them to jensenwb@ucmail.uc.edu

2010 Update

Pierre de Menten has supplied the author with some additional early references on the use of R in chemical formulas which nicely fill in the gap separating Guyton de Morveau from Gerhardt. The most important of these occur in the writings of Berzelius, who introduced the letter R into his new alphabetic chemical symbolism as an abbreviation for any "radical combustible" (in the original sense of Guyton) in the new preface which he added to the 1819 French translation of his work "Försök till en theoretisk åsift af läran om de kemiska proportionerna, samt af elektricitetens inflytelse såsom kemiskt agens" (Essay on the Theory of Chemical Proportions and on the Chemical Influences of Electricity) and which had first appeared the previous year in volume 3 of his famous *Lärbok i Kemien*. Berzelius used this abbreviation in the 1819 translation and later editions to write generalized formulas for various oxides, such as R + O, R + 2O, R + 3O, etc., in which R usually stood for a simple radical or chemical element. It is this particular usage, albeit slightly modernized, which is found in the later writings of Laurent and Mendeleev cited in the original column.

De Menten also notes that, prior to the publication of the *Précis* of 1844, Gerhardt sporadically used R to represent compound hydrocarbon radicals in his 1840-1842 translation of Liebig's *Traité de chimie organique*. All of this, in combination with Gerhardt's definition of R as representing "les eléments combustibles," strongly suggests that Gerhardt was still using the term and symbol in the Guyton-Berzelius sense as a symbol for any atom or collection of atoms capable of forming an oxide and not in the modern sense of exclusively representing a reactive fragment of a neutral hydrocarbon molecule.

Indeed, it would appear that this latter usage did not become exclusive until the early 20th century and the disappearance of the generalized oxide and hydride formulas at the top of most periodic tables. Its transitional nature in the late 19th century is well illustrated by van't Hoff, who used R extensively in his famous pamphlet of 1874 on the stereochemistry of the tetrahedral carbon atom and also in his far less successful 1884 monograph *Ansichten über die organische Chemie* in the same sense as Cannizzaro to represent not just alkyl groups, but any "generalized univalent group"

whether it was monoatomic or polyatomic, including halides, the hydroxyl group, the amine group, etc.

1. J. J. Berzelius, *Essai sur la théorie des proportions chimiques et sur l'influence chimique de l'électricité*, Méquignon-Marvis: Paris, 1819, p. xii.

2. J. H. van't Hoff, *Voorstel Tot Uitbreiding der Tegenwoordig in de Scheikunde Gebruikte Structuur-Formules in de Rumite*, Greven: Utrecht, 1874, pp. 4-5, 11, plate.

3. J. H. van't Hoff, *Ansichten über organische Chemie*, Vieweg: Braunschweig, 1884.