# **What is an organic substance?**



**Lee J. Silverberg[1](http://orcid.org/0000-0002-7353-1289)**

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# **Abstract**

No exact defnition of an "organic" substance has been agreed upon by the chemical community and textbook defnitions vary substantially. The question of what exactly constitutes an "organic" substance is explored in this paper. Various carbon-containing substances that have been by some considered to be "inorganic" are examined in an attempt to ascertain whether carbon in these compounds display diferent *chemical* behavior than what is expected of carbon in an "organic" substance. Types of substances considered are carbon allotropes, carbides, carbonates and bicarbonates, cyanide and cyanate ions, carbido clusters, carbon oxides, and compounds without hydrogen.

## **Graphic abstract**



Drawn By Carrie Silverberg

**Keywords** Organic · Inorganic · Organometallic · Carbon · Nomenclature

 $\boxtimes$  Lee J. Silverberg ljs43@psu.edu

<sup>1</sup> Pennsylvania State University, 200 University Drive, Schuylkill Haven, State College, PA 17972, USA

### **Introduction**

In the early history of modern chemistry, compounds that came from living things were thought to contain a "vital force" and were referred to as "organic" while those that were from nonliving materials such as minerals were called "inorganic" (McMurry [2016](#page-7-0)). It was believed that "inorganic" compounds could not be converted into "organic" compounds. This was disproven by Wöhler in 1828, when he converted ammonium cyanate to urea (Wöhler [1828](#page-7-1)). This, of course, rendered this nomenclatural distinction obsolete.

However, in the 193 years since Wöhler's discovery, the distinction between "organic" and "inorganic" substances has not been agreed upon. The International Union of Pure and Applied Chemistry (IUPAC), which is the body that is considered the authority on chemical nomenclature, does not give defnitions of "inorganic" or "organic," and in fact states that "the boundaries between 'organic' and 'inorganic' compounds are blurred" (Hartshorn et al. [2015\)](#page-6-0). This is rather surprising when one considers all the areas of nomenclature in which IUPAC does set out precise guidelines. Nonetheless, one recent frst-year undergraduate General Chemistry text notes that "a single, precise defnition" of an organic compound "has yet to be identifed by the chemistry community" (Flowers et al. [2015](#page-6-1)).

Second-year Organic Chemistry textbooks typically begin by introducing the feld to be studied by attempting to defne it. Clearly, the defnition is considered important pedagogically, however, it seems to be mainly a matter of opinion. This can be seen to be true by the various defnitions of "organic" substances found in frst- and second-year undergraduate textbooks, some examples of which include: a) "carbon compounds" (McMurry [2016\)](#page-7-0); (b) compounds "composed primarily of carbon and hydrogen," a defnition that "leaves considerable room for interpretation" (Karty [2014\)](#page-6-2); (c) "compounds that contain carbon and hydrogen, although many organic compounds… do not contain hydrogen" (Burdge and Overby [2012\)](#page-6-3); (d) "carbon-containing..." including "hydrogen  $(H<sub>2</sub>)$ —a kind of honorary organic molecule even though it doesn't contain carbon" (Jones and Fleming [2014\)](#page-6-4); e) "compounds of carbon, specifcally, those that contain hydrogen and often oxygen, nitrogen, and a few other elements" (Silberberg [2012\)](#page-7-2); f) "carbon-containing compounds" except for "a few compounds… such as its oxides and carbonates" (Zumdahl and Zumdahl [2012\)](#page-7-3); g) "any compound of carbon other than a carbonate, bicarbonate, cyanide, cyanate, carbide, or gaseous oxide" (Jesperson et al. [2012](#page-6-5)); h) "carbon compounds" except for "certain carbon compounds which are obtained from mineral sources… These are…" carbonates, bicarbonates, carbides, cyanides, and oxides (Madan [2013\)](#page-7-4); and i) those that "contain one or more carbon atoms" except for "substances such as diamond, graphite, carbon dioxide, ammonium cyanate, and sodium carbonate" which "are derived from minerals and have typical inorganic properties" (Wade [2013\)](#page-7-5).

Thus, it can be seen that certain carbon-containing substances have been considered "inorganic" primarily because either a) they are sourced from minerals, which is essentially following the old pre-Wöhler defnition of "inorganic;" or b) do not contain hydrogen. These exceptions do not base the distinction on chemical properties of the carbon in the substance, but simply on source or empirical formula. Some of these have "typical inorganic properties" (Wade [2013\)](#page-7-5), itself a nebulous concept that presumably refers to properties such as high melting point, water solubility, and high density; however, some do not. There is no unifying concept as to when a carbon compound should be considered "inorganic."

But why does this matter? The language of chemistry is important (Mosher [2017\)](#page-7-6). A pdf download of the latest IUPAC "Gold Book" (Compendium of Chemical Terminology),

a book of defnitions used in chemistry, is a whopping 1670 pages (Miloslav et al. [2014](#page-7-7)). The latest IUPAC "Blue Book" (Nomenclature of Organic Chemistry) print edition is 1568 pages (Favre and Powell [2013](#page-6-6)), while the most recent "Red Book" (Nomenclature of Inorganic Chemistry) adds another 378 pages (Connelly et al. [2005](#page-6-7)). There are other "color books" as well, but just sticking to those pertinent to "organic" and "inorganic" chemistry, there is a total of 3616 pages dedicated to helping chemists be very clear when communicating.

Still, in all this there is no clear defnition of "organic" that we can teach to students. Further, this is not only important specifcally to the two felds of "organic" and "inorganic" chemistry, but also to cross-disciplinary felds involving these. For example, "organometallic" compounds have been defned as those with "metal—carbon bonds," whereas in a "metal—organic compound… the organic fragment is bound only by metal-heteroatom bonds" (Crabtree [2005](#page-6-8)). Both are compounds with an "interaction between inorganic metal species and organic molecules" (Crabtree [2005](#page-6-8)). Thus, the identification of a compound as "organometallic" or "metal—organic" also relies on knowing what is or isn't an "organic" substance.

Without any clear rationale as to when carbon should be considered "organic" or "inorganic," it was hoped that one might be found by examining chemical properties. In the discussion below, various carbon-containing substances that have been by some considered to be "inorganic" are reviewed in an attempt to ascertain whether carbon in these compounds behaves diferently than what is expected of carbon in an "organic" substance.

# **Discussion**

#### **Allotropes of carbon**

Graphene is a planar sheet of interconnected, conjugated  $sp<sup>2</sup>$  carbons (Allen et al. [2010](#page-6-9)). It possesses aromaticity (Popov et al. [2012;](#page-7-8) Zdetsis and Economou [2015](#page-7-9)). The basal (interior) carbons undergo addition reactions across  $C = C$ , although high energies are required. The edge carbons, which are more tetrahedral and more reactive, can form benzyne or carbene intermediates (Wang and Shi [2015\)](#page-7-10).

Graphite is comprised of sheets of graphene stacked on top of each other. Graphite looks like a mineral, and is often considered "inorganic" (Alyea et al. [1968\)](#page-6-10). This view is perhaps bolstered by the fact that many intercalation compounds, in which a material is sandwiched in between graphene layers, are known (Enoki et al. [2003](#page-6-11)). However, graphite reacts with strong oxidizing agents to produce mellitic acid (Fig. [1](#page-2-0)) (Juettner [1937](#page-6-12)). Higher polyaromatic hydrocarbons (PAHs) similarly undergo radical oxidation to give mellitic

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acid (Benner et al [2000](#page-6-13)). "Aging" of graphite in humid air produces surface phenols and carboxylic acids (Boehm [2012\)](#page-6-14).

Carbon Black is comprised of "concentrically arranged, graphite-like crystallites… which can be considered as a highly disordered form of graphitic carbon. By heating to 3000 °C under inert conditions it develops into an ordered graphitic formation" (Orion Engineered Carbons [2015](#page-7-11)). There are various oxygen-containing functional groups on the surface, which "react in a similar way as the corresponding groups of the (sic) organic chemistry do" (Donnet [1982](#page-6-15)).

The curved allotropes known as fullerenes are also networks of  $sp<sup>2</sup>$  carbons, although each is somewhat pyramidalized due to the curvature of the molecule. The molecules react mainly by addition reactions to relieve the strain (Yamada et al. [2013;](#page-7-12) Bühl and Hirsch [2001;](#page-6-16) Balch and Olmstead [1998;](#page-6-17) Matsuo and Nakamura [2008](#page-7-13); Tzirakis and Orfanopoloulos [2013](#page-7-14)). York has discussed the chemistry of "inorganic fullerenes" – those comprised of elements other than carbon; this implies carbon fullerenes are "organic" (York [2004](#page-7-15)).

Diamond is one of the hardest materials known (Kraus and Slawson [1939](#page-6-18); Pan et al. [2009\)](#page-7-16), which would seem like a "typical inorganic" physical property. It is a network of tetrahedral  $sp<sup>3</sup>$  carbons, held together in a rigid structure of six-membered rings in chair conformations, the most stable conformation of six-membered rings found in "organic" compounds. However, the surface of diamond, both synthetic and natural, is reactive and able to form functional groups, such as carboxylic acids, anhydrides, lactones, alcohols, and others including R–N and R–S bonds (Boehm, [1966;](#page-6-19) Jiang and Xu, [1995;](#page-6-20) Dandekar et al. [1998;](#page-6-21) Azambre et al. [2005](#page-6-22); Frezzotti, [2019\)](#page-6-23).

#### **Other mineral‑like carbon compounds**

Covalent silicon carbide (SiC) is made up of  $sp<sup>3</sup>$  silicon and carbon atoms, each with four bonds, and is very hard, like diamond (Pedersen et al. [2012\)](#page-7-17). When the surface is cleaned by oxidation followed by removal of  $SiO<sub>2</sub>$  with HF, surface hydroxyls remain on carbon and silicon (Alekseev et al. [2017](#page-5-0)). These can be functionalized as ethers or acetals by reaction with groups such as alkenes (Alekseev et al. [2017\)](#page-5-0) or alkynes (Pujari, et al. [2013](#page-7-18)). Intriguingly, Alekseev suggests the possibility that strained surface carbons may be reacting with alkenes by addition of two surface carbons to the  $C = C$  with breakage of a  $\sigma$  bond between the surface carbons (Alekseev et al. [2017\)](#page-5-0).

Ionic calcium carbide  $(CaC_2)$  contains two *sp*-hydridized carbons in an acetylide dianion and behaves as such; addition of  $D_2O$  to calcium carbide gives deuterated acetylene (Hansen et al. [1986\)](#page-6-24).

The transition metal carbides (TMCs) are less clear-cut because of the bulk nature of many of the materials (Hwu and Chen [2005\)](#page-6-25), but display M-C bonding whether the carbon is "interstitial" or part of a more complex crystal structure such as in  $Fe<sub>3</sub>C$  (Häglund et al. [1993\)](#page-6-26), which would make them "organometallic" (Crabtree [2005](#page-6-8)).

In metal carbonates, e.g.  $Ca^{2+}(CO_3^{2-})$ , and bicarbonates,  $M^+(HCO_3^-)$ , the carbon is  $sp<sup>2</sup>$ -hybridized and bonded to three oxygens. The carbonate and bicarbonate ions are deprotonated forms of carbonic acid  $(H_2CO_3)$ , which by prior definitions is "organic" (e.g. contains hydrogen, is not part of a mineral, does not have so-called "inorganic properties"). The ions are part of living systems, which by the old Wöhler defnition would make them organic. The bicarbonate ion is part of the bicarbonate bufer system that regulates the pH of blood plasma (Krieg et al. [2014](#page-7-19)). Calcium carbonate is the primary component of eggshells (Butcher and Miles, [2020\)](#page-6-27) and seashells (Kinard [1980](#page-6-28)).



<span id="page-4-0"></span>**Fig. 2** Reppe reaction (hydroformylation) (Crabtree [2005](#page-6-8))



<span id="page-4-1"></span>Fig. 3 Formation of *N*-alkylcarbamates using DBU-CO<sub>2</sub> complex (Pérez et al. [2002\)](#page-7-25)

The cyanide ion (−CN) is an *sp*-hybridized carbanion and is very commonly used as a nucleophile in substitution reactions (Smith [2007\)](#page-7-20), a subject taught in second-year undergraduate organic chemistry. The cyanate ion ( $\overline{O}$ –C $\equiv$ N) can act as a nucleophile in S<sub>N</sub>1 or  $S_N$ 2 reactions to give cyanates or isocyanates, respectively (Holm and Wentrup [1966\)](#page-6-29).

#### **Carbido clusters**

Metal carbido clusters are known in which 5- or 6-coordinate carbon can be found (Crabtree [2005;](#page-6-8) Takemoto and Matsuzaka [2012](#page-7-21)). However, hypervalent carbon is not restricted to compounds where carbon is interacting with transition metals. Hypervalent carbocations are a well-known motif in organic chemistry, where they are often referred to as "nonclassical" carbocations (Olah [2001;](#page-7-22) Malischewski and Sepelt [2017\)](#page-7-23).

### **Carbon oxides**

Carbon monoxide and carbon dioxide are both gases at standard temperature and pressure, so they are not mineral-like in appearance, but they do lack hydrogen. However, they also are found within living systems (Berg et al. [2001](#page-6-30)).

Carbon monoxide (CO) is an unusual neutral carbon compound in that it has a lone pair on the *sp*-hybridized carbon. It will form M-C bonds with many transition metals; transition metal carbonyls are considered "organometallic" (Crabtree [2005](#page-6-8)) and can act as catalysts in carbonylation of "organic" compounds, for example in the Reppe hydroformylation reaction in which CO is a reactant and  $Fe(CO)$ <sub>5</sub> is a catalyst (Fig. [2\)](#page-4-0) (Crabtree [2005](#page-6-8)).

Carbon dioxide  $(CO<sub>2</sub>)$  also has an *sp*-hybridized carbon, which is electrophilic, as expected of a carbonyl. It undergoes many reactions with nucleophiles to give organic products (Sakakura et al. [2007](#page-7-24)). It can, for example, form a complex with bases such as diazabicycloundecene (DBU), which can then be used to form *N*-alkylcarbamates (Fig. [3](#page-4-1)) (Pérez et al. [2002](#page-7-25)). Second-year undergraduate organic chemistry texts commonly include the reaction of Grignard reagents with  $CO<sub>2</sub>$ .

### **Lack of hydrogen**

Many other carbonaceous molecules have no hydrogens but display typical "organic" behavior. For example, carbon tetrachloride  $(CCl<sub>4</sub>)$  is a "suitable organic solvent in different organic reactions," and can be used as an electrophilic chlorinating agent in reactions with carbanions (Abele and Lukevics [1999](#page-5-1)). Another important example is tetrafuoroethylene  $(F_2C=CF_2)$ , the monomer used to make polytetrafluoroethylene (PTFE) via free-radical polymerization, a standard organic mechanism.

# **Conclusion**

Currently, although we use the terms "organic" and "inorganic," the defnitions are fuzzy to say the least. When carbon has been considered "inorganic," it seems to be mainly because of physical properties or whether there is a hydrogen atom present. However, based on the evidence in the literature, it can be seen that carbon atoms, whether part of an allotrope, polyatomic ion, salt, purely covalent compound, metal carbide, or transition metal complex, and with or without hydrogen, display the same fundamental *chemical* behavior. It is suggested here that it is appropriate therefore to consider all carbon-containing substances "organic," at least in part. Transition metal complexes can be considered as being "organometallic," or "metal–organic." When carbon is part of an ionic compound, it can be viewed as a salt of an "organic ion." Compounds that do not contain carbon would be considered "inorganic." These defnitions would clarify what chemists mean when using these terms, and increase understanding when chemists communicate. They would take the terminology out of the realm of opinion and into a sound theoretical basis. Students would fnally be given a concrete defnition that would be consistent, irrespective of source. For researchers, the consistency of the chemical behavior of carbon shown here should help break down artifcial barriers between how chemists in the various sub-disciplines think about carbon and its chemistry, ultimately leading to a more unifed approach to carbon chemistry.

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