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Abstract

No exact definition of an "organic" substance has been agreed upon by the chemical community and textbook definitions 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 different *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

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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). 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). 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 definitions of "inorganic" or "organic," and in fact states that "the boundaries between 'organic' and 'inorganic' compounds are blurred" (Hartshorn et al. 2015). This is rather surprising when one considers all the areas of nomenclature in which IUPAC does set out precise guidelines. Nonetheless, one recent first-year undergraduate General Chemistry text notes that "a single, precise definition" of an organic compound "has yet to be identified by the chemistry community" (Flowers et al. 2015).

Second-year Organic Chemistry textbooks typically begin by introducing the field to be studied by attempting to define it. Clearly, the definition is considered important pedagogically, however, it seems to be mainly a matter of opinion. This can be seen to be true by the various definitions of "organic" substances found in first- and second-year undergraduate textbooks, some examples of which include: a) "carbon compounds" (McMurry 2016); (b) compounds "composed primarily of carbon and hydrogen," a definition that "leaves considerable room for interpretation" (Karty 2014); (c) "compounds that contain carbon and hydrogen, although many organic compounds... do not contain hydrogen" (Burdge and Overby 2012); (d) "carbon-containing..." including "hydrogen (H_2)—a kind of honorary organic molecule even though it doesn't contain carbon" (Jones and Fleming 2014); e) "compounds of carbon, specifically, those that contain hydrogen and often oxygen, nitrogen, and a few other elements" (Silberberg 2012); f) "carbon-containing compounds" except for "a few compounds... such as its oxides and carbonates" (Zumdahl and Zumdahl 2012); g) "any compound of carbon other than a carbonate, bicarbonate, cyanide, cyanate, carbide, or gaseous oxide" (Jesperson et al. 2012); h) "carbon compounds" except for "certain carbon compounds which are obtained from mineral sources... These are..." carbonates, bicarbonates, carbides, cyanides, and oxides (Madan 2013); 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).

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 definition 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), 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). A pdf download of the latest IUPAC "Gold Book" (Compendium of Chemical Terminology),

a book of definitions used in chemistry, is a whopping 1670 pages (Miloslav et al. 2014). The latest IUPAC "Blue Book" (Nomenclature of Organic Chemistry) print edition is 1568 pages (Favre and Powell 2013), while the most recent "Red Book" (Nomenclature of Inorganic Chemistry) adds another 378 pages (Connelly et al. 2005). 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 definition of "organic" that we can teach to students. Further, this is not only important specifically to the two fields of "organic" and "inorganic" chemistry, but also to cross-disciplinary fields involving these. For example, "organometallic" compounds have been defined as those with "metal—carbon bonds," whereas in a "metal—organic compound… the organic fragment is bound only by metal-heteroatom bonds" (Crabtree 2005). Both are compounds with an "interaction between inorganic metal species and organic molecules" (Crabtree 2005). 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 differently than what is expected of carbon in an "organic" substance.

Discussion

Allotropes of carbon

Graphene is a planar sheet of interconnected, conjugated sp^2 carbons (Allen et al. 2010). It possesses aromaticity (Popov et al. 2012; Zdetsis and Economou 2015). 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 carbone intermediates (Wang and Shi 2015).

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). 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). However, graphite reacts with strong oxidizing agents to produce mellitic acid (Fig. 1) (Juettner 1937). Higher polyaromatic hydrocarbons (PAHs) similarly undergo radical oxidation to give mellitic

Fig. 1 Mellitic acid



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acid (Benner et al 2000). "Aging" of graphite in humid air produces surface phenols and carboxylic acids (Boehm 2012).

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). 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).

The curved allotropes known as fullerenes are also networks of sp^2 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; Bühl and Hirsch 2001; Balch and Olmstead 1998; Matsuo and Nakamura 2008; Tzirakis and Orfanopoloulos 2013). York has discussed the chemistry of "inorganic fullerenes" – those comprised of elements other than carbon; this implies carbon fullerenes are "organic" (York 2004).

Diamond is one of the hardest materials known (Kraus and Slawson 1939; Pan et al. 2009), which would seem like a "typical inorganic" physical property. It is a network of tetrahedral sp^3 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; Jiang and Xu, 1995; Dandekar et al. 1998; Azambre et al. 2005; Frezzotti, 2019).

Other mineral-like carbon compounds

Covalent silicon carbide (SiC) is made up of sp^3 silicon and carbon atoms, each with four bonds, and is very hard, like diamond (Pedersen et al. 2012). When the surface is cleaned by oxidation followed by removal of SiO₂ with HF, surface hydroxyls remain on carbon and silicon (Alekseev et al. 2017). These can be functionalized as ethers or acetals by reaction with groups such as alkenes (Alekseev et al. 2017) or alkynes (Pujari, et al. 2013). Intriguingly, Alekseev suggests the possibility that strained surface carbons may be reacing with alkenes by addition of two surface carbons to the C=C with breakage of a σ bond between the surface carbons (Alekseev et al. 2017).

Ionic calcium carbide (CaC_2) contains two *sp*-hydridized carbons in an acetylide dianion and behaves as such; addition of D₂O to calcium carbide gives deuterated acetylene (Hansen et al. 1986).

The transition metal carbides (TMCs) are less clear-cut because of the bulk nature of many of the materials (Hwu and Chen 2005), but display M-C bonding whether the carbon is "interstitial" or part of a more complex crystal structure such as in Fe₃C (Häglund et al. 1993), which would make them "organometallic" (Crabtree 2005).

In metal carbonates, e.g. $Ca^{2+}(CO_3^{2-})$, and bicarbonates, $M^+(HCO_3^{-})$, the carbon is sp^2 -hybridized and bonded to three oxygens. The carbonate and bicarbonate ions are deprotonated forms of carbonic acid (H₂CO₃), 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 definition would make them organic. The bicarbonate ion is part of the bicarbonate buffer system that regulates the pH of blood plasma (Krieg et al. 2014). Calcium carbonate is the primary component of eggshells (Butcher and Miles, 2020) and seashells (Kinard 1980).



Fig. 2 Reppe reaction (hydroformylation) (Crabtree 2005)



Fig. 3 Formation of *N*-alkylcarbamates using DBU-CO₂ complex (Pérez et al. 2002)

The cyanide ion (^{-}CN) is an *sp*-hybridized carbanion and is very commonly used as a nucleophile in substitution reactions (Smith 2007), a subject taught in second-year undergraduate organic chemistry. The cyanate ion ($^{-}O-C\equiv N$) can act as a nucleophile in S_N1 or S_N2 reactions to give cyanates or isocyanates, respectively (Holm and Wentrup 1966).

Carbido clusters

Metal carbido clusters are known in which 5- or 6-coordinate carbon can be found (Crabtree 2005; Takemoto and Matsuzaka 2012). 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; Malischewski and Sepelt 2017).

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).

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) and can act as catalysts in carbonylation of "organic" compounds, for example in the Reppe hydroformylation reaction in which CO is a reactant and $Fe(CO)_5$ is a catalyst (Fig. 2) (Crabtree 2005).

Carbon dioxide (CO_2) 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). It can, for example, form a complex with bases such as diazabicycloundecene (DBU), which can then be used to form *N*-alkylcarbamates (Fig. 3)

(Pérez et al. 2002). Second-year undergraduate organic chemistry texts commonly include the reaction of Grignard reagents with CO_2 .

Lack of hydrogen

Many other carbonaceous molecules have no hydrogens but display typical "organic" behavior. For example, carbon tetrachloride (CCl₄) 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). Another important example is tetrafluoroethylene ($F_2C=CF_2$), 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 definitions 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 definitions 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 finally be given a concrete definition that would be consistent, irrespective of source. For researchers, the consistency of the chemical behavior of carbon shown here should help break down artificial barriers between how chemists in the various sub-disciplines think about carbon and its chemistry, ultimately leading to a more unified approach to carbon chemistry.

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