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# MECHANO(-)SYNTHESIS

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## DEFINITION

Mechano(-)synthesis refers a hypothetical chemical synthesis in which reaction outcomes are determined by the use of mechanical constraints to direct reactive molecules to specific molecular sites. In a Mech-synth process reactive molecules would be attached to molecular mechanical systems, and their encounters would result from mechanical motions bringing them together in planned sequences, positions, and orientations. Mech-synth strongly favoring desired reactions by holding reactants together in optimal orientations for many molecular vibration cycles. In biology, the ribosome provides an example of a programmable Mech-synth device. There are presently no chemical syntheses which fully achieve this aim. Some atomic placement has been achieved with scanning tunnelling microscopes.

## KEYWORDS:

Hypothetical chemical synthesis; Driven chemical reaction; Mechanochemistry; Molecular engineering; Molecular manufacturing

## HISTORICAL ORIGIN(S)

In conventional chemical synthesis or chemosynthesis, reactive molecules encounter one another through random thermal motion in a liquid or vapour, while Mech-synth aim is to position molecules in specific locations in a carefully chosen sequence. By holding and positioning molecules, controlling thus how the molecules react, building up complex structures with atomically precise control.

Mech-synth is inspired from biology. It is known that the ribosome is a complex molecular machine found within all living cells that serves as the site of biological protein synthesis (translation). Ribosomes link amino acids together in the order specified by messenger RNA (mRNA) molecules. From here it has been binged out the idea that is possible to synthesize chemical products by using only mechanical action. A special issue of Chemical Society Reviews (issue 18, volume 42, 2013) was dedicated to the theme of mechanochemistry.

## NANO-SCIENTIFIC DEVELOPMENT(S)

In the early times, Theophrastus of Eresus, an Aristotle's student wrote in about 315 B.C. a short booklet titled "On Stones" (the earliest surviving document related to chemistry) containing a reference on the reduction of cinnabar to mercury by grinding in a copper mortar with a copper pestle (Takacs, 2013).

Much later, in 1820, Faraday described the reduction of silver chloride by grinding with zinc, tin, iron, and copper in a mortar (Faraday, 1820), but the first systematic studies of Mech-synth reactions were carried out at the end of the $19^{th}$ century (Spring, 1883; Lea, 1892) while the first documented application of mechanical stimulus to induce chemical reactions in organic systems is probably (Ling & Baker, 1893).

The beginning of the Mech-synth era can be considered when the technique of moving single atoms mechanically was firstly proposed (Drexler, 1986).

The principle of Mech-synth is relatively simple (see Figure 1) but the implementation of the principle is difficult, due to the scale (atomic scale).

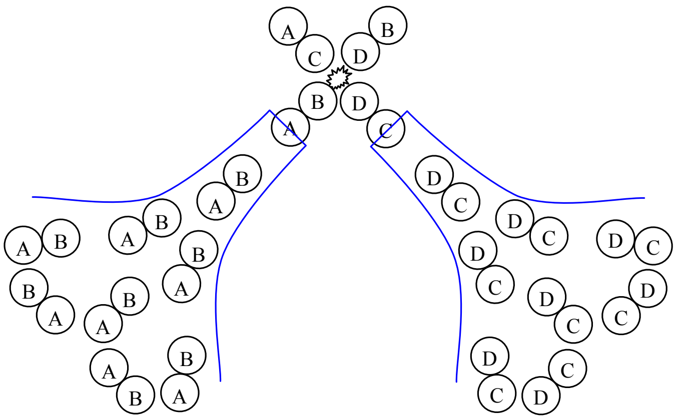

**Figure 1.** Mech-synth for driven substitution reaction

It should be noted that the term mechanochemistry is sometimes confused with mechanosynthesis, which refers specifically to the machine-controlled construction of complex molecular products (Drexler, 1992). The principle of Mech-synth is relatively simple (see Figure 1) but the implementation of the principle is difficult, due to the scale (atomic scale). Since it is a typical machine-driven process, its use implies manipulation of manufacturing concepts, such as is exemplified in Table 1 (adapted from Table 1.1 from Drexler, 1991).

**Table 1.** Scale differences between conventional, miniaturized, chemistry, biochemistry, and molecular manufacturing.

| Characteristic | Conventional | Miniaturized | Biochemistry | Chemistry | Mech-synth |
|---|---|---|---|---|---|
| Molecular precision | No | No | Yes | Yes | Yes |
| Positional control | Yes | Yes | Some | No | Yes |
| Feature scale | 1 mm | 1 µm | 0.3 nm | 0.3 nm | 0.3 nm |
| Product scale | 1 m | 10 mm | 10 nm | 1 nm | 1 µm |
| Defect rate | $10^{-4}$ | $10^{-7}$ | $10^{-11}$ | $10^{-2}$ | $10^{-12}$ |
| Producing time | $10^{1}$ s | $10^{2}$ s | $10^{-3}$ s | $10^{3}$ s | $10^{-6}$ s |
| Output content | materials & shapes | | monomer sequences | atoms & bonds | |

To work at molecular level, the devices should be at same scale. Therefore, it is a strong connection between Mech-synth and molecular machines concept. Most of the explorations to build Mech-synth have focused on using carbon, because it allows the building of structures of large size and finds its uses in medical and mechanical applications.

## Nano-Chemical Application(s)

There is a growing body of studies for synthesizing diamond by mechanically removing/adding hydrogen atoms (Temelso et al., 2006) and depositing carbon atoms (De Federico & Jaime, 2006; Yin et al., 2007). Other applications include constructing of metal layers - sulfate intercalated Mg-Al layered double hydroxides (Mg-Al-$SO_4$-LDH) was successfully synthesized by the one step mechanochemical activation method followed by subsequent water washing and aging in (Fahami & Beall, 2016), formation of highly incompressible and hardness materials - the formation of rhenium carbide ($Re_2C$) from the elements was reported from mechanochemical treatment after 640 min of milling in (Granados-Fitch & al. 2016), the formation of soft magnetic materials - soft magnetic $Fe_3O_4$/$Ni_3Fe$ composite powder has been synthetized starting from Fe, Ni and $Fe_2O_3$ powders via mechanosynthesis and subsequent annealing in (Marinca et al., 2015).

In regard with the diamond synthesis (Freitas & Merkle, 2008) proposes a minimal toolset (C/Ge/H DMS) for positional diamond mechanosynthesis consisting from three primary tooltypes and six auxiliary ones (see Figure 2, adapted from Freitas & Merkle, 2008) requiring system requiring only four simple feedstock molecules - $CH_4$ (methane) and $C_2H_2$ (acetylene) as the carbon sources, $Ge_2H_6$ (digermane) as the germanium source, and $H_2$ as a hydrogen source.

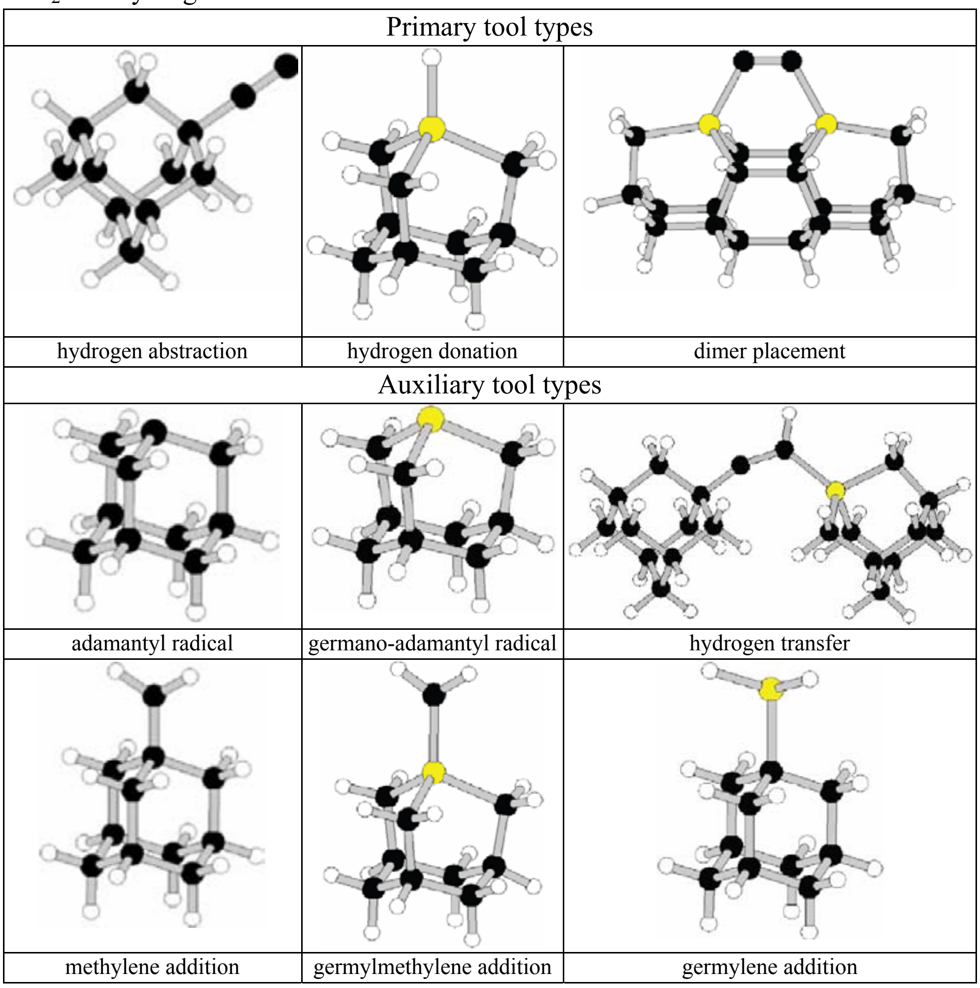


**Figure 2.** Minimal toolset for positional diamond Mech-synth

## MULTI-/TRANS- DISCIPLINARY CONNECTION(S)

To arrive at a Mech-synth one must use computational modelling, and here strict motion constraints reduce the number of configurations that must be examined, and because reactions that consume high-energy species can have large thermodynamic driving forces, making predicted behaviours relatively insensitive to errors in calculated model energies, leaving therefore a little room for computations at reasonable level of theory. Engineering of controlled processes passes the Mech-synth through the chemical engineering and finally the applications of the products includes materials science where commonly these are tested.

## OPEN ISSUES

The goal of one line of Mech-synth research focuses on overcoming the problems by calibration, and selection of appropriate synthesis reactions. Some suggests include attempting to develop a specialized, very small machine tool that can build copies of it under the control of an external computer. In the literature, such a tool is called an assembler or molecular assembler. Once assemblers exist, geometric growth (directing copies to make copies) could reduce the cost of assemblers rapidly. Control by an external computer should then permit large groups of assemblers to construct large, useful projects to atomic precision. One such project would combine molecular-level conveyor belts with permanently mounted assemblers to produce a factory.

To manage the risk coming from various potential disasters arising from runaway replicators which could be built using mechanosynthesis, the UK Royal Society and UK Royal Academy of Engineering in 2003 commissioned a study to deal with these issues and larger social and ecological implications, led by mechanical engineering professor Ann Dowling. This was anticipated by some to take a strong position on these problems and potentials and suggest any development path to a general theory of so-called mechanosynthesis. It should be noted that current technical proposals for nanofactories do not include self-replicating nanorobots, and recent ethical guidelines would prohibit development of unconstrained self-replication capabilities in nanomachines.

## RELATED LIST OF ABBREVIATIONS

DMS acronym is used for diamante mechano-synthesis.

## REFERENCES AND FURTHER READING

Takacs, L.; 2013. The historical development of mechanochemistry. Chem. Soc. Rev. 42: 7649-7659.

Faraday, M.; 1820. Extracts, method of preparing, by evaporation in vacuo, on the decomposition of chloride of silver by hydrogen and by zinc. Q. J. Sci. Lit. Arts 8: 374-375.

Spring W.; 1883. Formation d'Arséniures par la Pression Bull. Soc. Chim. Fr. 40: 195-196. Formation de Quelques Sulfures par l'Action de la Pression. Considérations qui en Découlent Touchant les Propriétés des États Allotropiques du Phosphore et du Carbone Bull. Soc. Chim. Fr. 40: 641-647.

Lea C.M.; 1892. Disruption of the Silver Haloid Molecule by Mechanical Force. Am. J. Sci. 43(3): 527-531.
Ling, A.R.; Baker, J.L.; 1893. Halogen derivatives of quinone. Part III. Derivatives of quinhydrone. J. Chem. Soc. Trans. 63: 1314-1327.
Drexler, E.K.; 1986. Engines of Creation: The Coming Era of Nanotechnology. New York: Anchor Books.
Drexler, E.K. 1992. Nanosystems: Molecular machinery, manufacturing and computation. Chichester: J. Wiley & Sons.
Drexler, E.K. 1991. Molecular machinery and manufacturing with applications to computation. PhD Thesis in the field of Molecular nanotechnology (PhD Advisor: Marvin L. MINSKY). Massachusetts Institute of Technology.
Temelso, B.; Sherrill, C.D.; Merkle, R.C.; Freitas, R.A.; 2006. High-level Ab Initio Studies of Hydrogen Abstraction from Prototype Hydrocarbon Systems. J. Phys. Chem. A 110 (38): 11160-11173.
Yin, Z.-X.; Cui, J.-Z.; Liu, W.; Shi, X.-H.; Xu, J.; 2007. Horizontal Ge-Substituted Polymantane-Based C2 Dimer Placement Tooltip Motifs for Diamond Mechanosynthesis. J. Comput. Theor. Nanosci. 4(7): 1243-1248.
Fahami, A.; Beall, G.W.; 2016. Mechanosynthesis and characterization of Hydrotalcite like Mg-Al-$SO_4$-LDH. Mater. Lett. 165: 192-195.
Granados-Fitch, M.G.; Juarez-Arellano, E.A.; Quintana-Melgoza, J.M.; Avalos-Borja, M.; 2016. Mechanosynthesis of rhenium carbide at ambient pressure and temperature. Int. J. Refract. Metal. Hard Mater. 55: 11-15.
Marinca, T.F.; Chicinaş, H.F.; Neamţu, B.V.; Isnard, O.; Chicinaş, I.; 2015. Structural, thermal and magnetic characteristics of $Fe_3O_4$/$Ni_3Fe$ composite powder obtained by mechanosynthesis-annealing route. J. Alloy. Compound. 652: 313-321.
Freitas Jr., R.A.; Merkle R.C.; 2008. A Minimal Toolset for Positional Diamond Mechanosynthesis. J. Comput. Theor. Nanosci. 5: 760-861.