

Mechanochemistry: an overview*

José F. Fernández-Bertran

Centro de Química Farmacéutica, PO Box 16042, La Habana, Cuba

Abstract: The field of mechanochemistry is reviewed. A large number of mechanochemical reactions are described as well as industrial applications.

INTRODUCTION

At the beginning of this century, W. Nernst classified the different fields of chemistry according to the type of energy supplied to the system: thermochemistry, electrochemistry, photochemistry, etc. The name mechanochemistry was applied to the field of reactions caused by mechanical energy. A narrower field, tribochemistry, was used for reactions generated by friction during the milling of solid reagents [1–3].

A variety of processes takes place on mechanical grinding of solids such as:

- (a) Conminution of the particles to a very small size.
- (b) Generation of large new surfaces.
- (c) Formation of dislocations and point defects in the crystalline structure.
- (d) Phase transformations in polymorphic materials.
- (e) Chemical reactions: decomposition, ionic exchange, oxidation-reduction, complex and adduct formation, etc.

The occurrence of these reactions was attributed to the heat generated in the milling process, favored by the large area of contact between the solids [1–3]. However, since the end of the last century, Carey Lee noticed that mechanochemical processes were different from thermal processes [1]. For example, heating of AgCl and HgCl leads to melting and subliming of these solids, while milling them produces their decomposition into Cl₂ gas and metal.

The role played by mechanical defects as high energy structures and its importance in chemical transformations was recognized later [3].

PECULIARITIES OF MECHANOCHEMICAL PROCESSES

The grinding of two solid substances generates a complex series of transformations, the mechanical energy breaking the order of the crystalline structure, producing cracks, and new surfaces. At the point of collision of the edges the solids deform and even melt, forming hot points where the molecules can reach very high vibrational excitation leading to bond breaking. These stochastic processes occur in a period of 10⁻⁷ s. in which thermal equilibrium does not exist [1].

This period, called the plasma phase, is followed by a post plasma period of 10⁻⁶ s. or more in which relaxation processes dissipate the energy reaching the Maxwell–Boltzmann distribution [1]. This post plasmonic reactions are responsible for many of the products formed.

Finally, the energy accumulated in the defects of the crystalline structure can lead to slower chemical processes. As we can see, mechanochemical reactions can be very complex processes.

*Plenary lecture presented at the 3rd International Congress of the Cuban Chemical Society, Havana, Cuba, 1–4 December 1998, pp. 559–586.

Correspondence: Fax: (537) 33 64 71, E-mail: cqf@infomed.sld.cu

MECHANOCHEMICAL REACTORS

Milling can be carried out in a variety of ways. The simplest is the laboratory mortar and pestle. This hand milling processes can provoke a large number of mechanochemical reactions which do not require surmounting a high energy barrier. Ball mills are used when higher energy is required and when the milling time involves hours or even days. Laboratory vibrators of the Wiggle-Bug type are very efficient in milling small samples.

Very high energy vibrators such as high speed attritors or stainless steel ball mills of high impact (Spex type) are used for prolonged high energy milling as in mechanical alloying or amorphization of hard crystalline solids [1–3]. Ultrasonic can also be used mechanochemically [4,5].

MONITORING MECHANOCHEMICAL PROCESSES

The best way to study mechanochemical transformations is to analyze *in-situ* the milled mixture using appropriate spectroscopic methods, since chemical handling can obscure the true nature of the initial products. Most common tools are IR and XRD techniques which normally allow the identification of the products.

In organic reactions, solid state NMR can be very useful and with Fe and Sn compounds, Mossbauer spectroscopy is most valuable. Other techniques like HREM, EXFAX and X-ray cyclotron resonance have been used to study the new surfaces [5,6]. In sophisticated experiments like reactions produced during crack formation, MS enables the determination of the gaseous products as in the decomposition of nitrates and bromates [7].

PHASE TRANSITIONS

Polymorphic materials have two or more phases which are stable in certain temperature and pressure range [8]. Examples are collected in Table 1. These phase changes are the simplest transformations that can be studied tribochemically. They have importance in geochemical studies as they give information on the geological processes of rocks [8]. They also allow the estimation of the pressures obtained during a milling process, which is very difficult to asses by other means. Due to the observed phase transitions, the pressure range reached by hand milling in a mortar can be estimated to be as high as 15 000 bars. It is possible to transform the stable low pressure form to the high pressure one by milling, if sufficient mechanical energy is available to overcome the activation barrier. Milling the high pressure form also leads to the appearance of the low pressure one, since milling provides a whole spectrum of pressures.

Table 1 Mechanochemical phase transformations

Substance	Low pressure form	High pressure form	Pressure (bars)
CaCO ₃	Calcite	Aragonite	3000
PbO ₂	I	II orthorhombic	10 000
Sb ₂ O ₃	Senarmonite	Valentinite	10 000
SiO ₂	Quartz	Coesite	13 500

MECHANOCHEMICAL REACTIONS IN KBR DISKS

IR spectra of solids are normally run, in pressed KBr disks [9]. Also used are KCl, CsBr and CsI salts as matrices. During the grinding and pressing processes, the analyte can undergo mechanochemical changes such as polymorphic transitions [8], ion exchange processes [10–14], complex formation [15–21] and oxidation-reduction reactions [22–25]. The chemists are not always aware of these transformations and many pitfalls have been reported in the literature concerning IR spectra of solids [26–30].

We will now illustrate several of these reactions.

Formation of solid solutions

When the analyte and KBr have similar structures, the milling can lead to the formation of solid solutions. The presence of moisture in the KBr or its absorption from the atmosphere during milling and pressing increases the diffusion of ions and facilitates the process. The cations and anions occupy the positions of K^+ and Br^- in the KBr network [10–13]. Other alkali halide matrices present the same phenomena. See Table 2.

Table 2 Mechanochemical formation of solid solutions in alkali halide matrices

Salt	Matrix
LiCl	NaCl
CsCl	NaBr
CsI	NaBr
NaBr	CsBr
NaCl	CsCl

Ionic exchange

Exchange of anions and cations with KBr leading to formation of new products can take place in the KBr disk when the ΔF of the reaction is negative as discussed by Milne [10–14]. A simple case is the formation of insoluble bromides as occur with Ag, Hg and Pb salts [9]. Examples are given in Table 3.

Table 3 Ionic exchange in KBr pressed disks

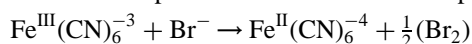
Salt	Final products
$CuSO_4 \times 5H_2O$	$CuK_2(SO_4)_2$, $CuK_2Br_2(SO_4)$
$PbSO_4$	$PbBr_2$, K_2SO_4
$AgNO_3$	$AgBr$, KNO_3
$Hg(NO_3)_2$	$HgBr_2$, KNO_3

Complex formation

KBr can form complexes with organic substances such as adducts with sugars [15–17], thiourea [18], succinimide [19] and pyridine oxide [20]. However, the nature of many of these complexes is not well established [9]. With $SnBr_4$, KBr forms the salt K_2SnBr_6 [21]. We are at present studying the reactions of alkali halides with sugars, the most promising salt being KF which forms crystalline adducts with mono and disaccharides, whose nature is now under study.

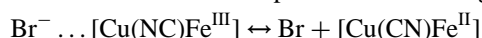
Oxidation-reduction reactions

Since the Br^- anion is a reducing agent, many analytes which are oxidants can be reduced during milling to obtain the pressed KBr disk. For example, all ferricyanides are reduced to ferrocyanides [22–25].



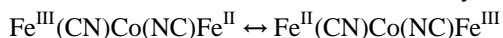
The velocity of the reaction depends strongly on the outer cation of the ferricyanide, for example [23]: $K \ll Zn < Mn, Co, Ni < Cu$.

This is related to the path of the reducing electron from the Br^- to the central Fe^{III} cation:



When the Br^- is bound to the outer transition metal cation, the bridge is established for electron transfer. Cu^{+2} with its possibility of taking the electron to form Cu^{+1} also speeds the process which ends with the electronic transmittion through the CN bond to Fe^{III} [23].

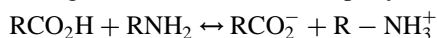
An interesting case occurs with Co^{+2} ferricyanide. The reduction to ferrocyanide goes through a stable intermediate, a mixed valence ferri-ferrocyanide complex [23].



The complex has been characterized by IR, XRD and Mossbauer spectroscopies [23].

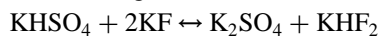
ACID-BASE REACTIONS

The reactions of organic acids with amines in the solid state have been studied in our laboratory [31]. Strong acids and bases react rapidly on milling to form ammonium salt.



Weak acids and bases can form stable hydrogen bonded complexes some of which are not stable in water solutions. We could not obtain amides even under the strongest mechanochemical conditions.

An interesting acid-base reaction takes place when acidic substances are milled with KF. This salt tends to form the acid fluoride anion HF_2^- and abstracts protons from salts such as KHSO_4 , ammonium salts and organic acids [32].



AMORPHIZATION OF POLYMERS

Macromolecules, natural or synthetic can exhibit crystalline regions due to association of the chains in short range order as in cellulose. This secondary structure is very important in the biological properties of the polymers. Milling in a mortar can disrupt the hydrogen bond interactions and amorphize the polymer. This happens with starch and polypeptides. The milling of enzymes destroys their biological properties [1].

Strong milling leads to the accumulation of mechanical energy in the long chains and strong bonds such as C–C, C–O and C–N can be ruptured. The phenomena can be detected by ESR due to the formation of free radicals. S–S bonds in proteins are easily broken. In synthetic polymers, milling can be used to create this broken bonds and react the product with other chemicals for grafting and modifying their physical properties [1].

INDUSTRIAL APPLICATIONS

We will now mention some specific applications of mechanochemistry in industry.

Mechano synthesis

Organic mechano synthesis is in its infancy but the possibility of carrying out reactions in the absence of solvent is a very attractive proposition. The processes are not only simpler and economical but also ecologically advantageous, eliminating the contamination of the surroundings with obnoxious chemicals. The implanting of pharmaceuticals on polymeric matrices for its transport in the organism is also a promising pharmaceutical field [33,34]. In the inorganic field there are experiences in the syntheses of alloys, cermets, spinels, semiconductors and superconductors, catalysts, fertilizer, ceramics construction materials, etc. [1,35].

Cold alloying

The milling at room temperature of two metals can lead to the production of alloys. The milling distorts the metallic particles to laminae and on further milling, diffusion leads to a homogenous alloy. Cold alloying is a rapidly expanding field [35].

Cermets

Milling a soft metal with a hard ceramic material leads to the formation of valuable composites with new important properties: the cermets.

On milling, the hard ceramic particles becomes imbedded in a metal host matrix. On further milling, the hard particles are micronized and the metal covers the fine ceramic units leading to spherical particles, the cermets [3,35].

Mechanical activation of minerals

Milling certain minerals alters their properties in ways that can be used in industry:

- 1 Silica, alumina and aluminosilicates can be activated to be valuable catalyst, with the incorporation of small amount of metals [1,2].
- 2 Bauxite can be activated by milling, allowing its extraction of $\text{Al}(\text{OH})_3$ by concentrated NaOH solutions at lower temperatures. This allows a purer $\text{Al}(\text{OH})_3$ to be obtained for Al production [1,2].
- 3 Phosphate rock, the main source of P in the fertilizer industry, can be amorphized under high mechanical impact, leading to a material that can be attacked by the plant roots. This new fertilizer, tribophos, is cheaper than those obtained by treating the mineral with sulfuric or phosphoric acid [1,2].
- 4 If instead of using sand and gravel in the concrete industry, the freshly ground rock is mixed with the cement and water, a very hard concrete results, superconcrete, with the cement phase strongly bound to the hard rock and sand phase [1,2].

Many more uses of mechanical activation will certainly be developed in the future.

REFERENCES

- 1 G. Heinicke. *Tribochemistry*. Akademic-Verlag, Berlin (1984).
- 2 K. Tkacova. *Mechanical Activation of Minerals*. Elsevier, Amsterdam (1989).
- 3 V. V. Boldyrev. *Solid State Ionics* **63–65**, 537 (1993).
- 4 K. S. Suslick, D. J. Casadonte. *J. Am. Chem. Soc.* **109**, 3459 (1987).
- 5 V. V. Boldyrev. *Ultrasonic Sonochem.* **2**, 143 (1995).
- 6 V. Boldyrev, E. Awwakumov, H. Harenz, G. Heinicke, L. Strugova. *Z. Anorg. Allg. Chem.* **393**, 152 (1972).
- 7 P. Fox, J. Loria-Rutz. *Proc. Roy. Soc. A* **317**, 79 (1970).
- 8 F. Dachille, R. Roy. *Nature* **186**, 71 (1960).
- 9 J. Fernandez-Bertran, E. Reguera. *Solid State Ionics* **93**, 139 (1997).
- 10 J. W. Milne. *Spectrochim. Acta* **32A**, 1347 (1976).
- 11 S. Yariv, S. Shoval. *Appl. Spectrosc.* **39**, 599 (1985).
- 12 I. Severin, H. J. Seifert, S. Yariv. *J. Solid State Chem.* **88**, 401 (1990).
- 13 V. W. Meloche, G. E. Kalbus. *J. Inorg. Nucl. Chem.* **6**, 104 (1957).
- 14 F. Vrátný. *J. Inorg. Nucl. Chem.* **10**, 328 (1959).
- 15 S. A. Barker, E. J. Bourne, W. B. Neely, D. H. Whiffin. *Chem. Ind. London* 1418 (1954).
- 16 V. C. Farmer. *Spectrochim. Acta* **8**, 374 (1957).
- 17 L. Segal. *Appl. Spectrosc.* **18**, 107 (1964).
- 18 J. E. Stuart. *J. Chem. Phys.* **26**, 248 (1957).
- 19 A. Tilk, H. J. van der Malen. *Chem. Weekblad* 53 (1957).
- 20 J. Padmos, A. van Veen. *Spectrochim. Acta* **38A**, 97 (1982).
- 21 W. Kutzelnigg, G. Nonnenmacher, R. Mecke. *Chem. Ber.* **93**, 1297 (1960).
- 22 J. Fernandez-Bertran, J. Blanco, M. Hernández. *Spectrochim. Acta* **43A**, 981 (1987).
- 23 J. Fernandez-Bertran, J. Blanco, M. Hernández, R. Rodríguez. *React. Solids* **5**, 95 (1988).

- 24 J. Fernandez-Bertran, A. Dago, R. Guardiola, J. Blanco. *React. Solids* **6**, 105 (1988).
- 25 E. Reguera, J. Frenandez, C. Díaz, S. Rondón. *Hyperf. Interact.* **53**, 391 (1990).
- 26 J. B. Ayres, W. H. Waggoner. *J. Inorg. Nucl. Chem.* **31**, 2045 (1969).
- 27 J. B. Ayres, W. H. Waggoner. *J. Inorg. Nucl. Chem.* **33**, 721 (1971).
- 28 A. N. Garg, P. S. Goel. *Inorg. Chem.* **10**, 1344 (1971).
- 29 D. Y. Parwate, A. N. Garg. *Indian J. Chem.* **25A**, 151 (1986).
- 30 N. E. Kob, J. E. House Jr. *Transit. Metal Chem.* **19**, 31 (1994).
- 31 J. Fernandez-Bertran, J. C. Alvarez, E. Reguera. *Solid State Ionics* **106**, 129 (1998).
- 32 J. Fernandez-Bertran, E. Reguera. *Solid State Ionics* (1998), accepted.
- 33 E. Reguera, J. Balmaseda, G. Quintana, A. Gomez, J. Fernandez-Bertran. *Polyhedron* **17**, 13 (1998).
- 34 F. Toda. *Synlett* 303 (1993).
- 35 L. Aymard, M. Figlarz. *Solid State Ionics* **63–65**, 143 (1993).