

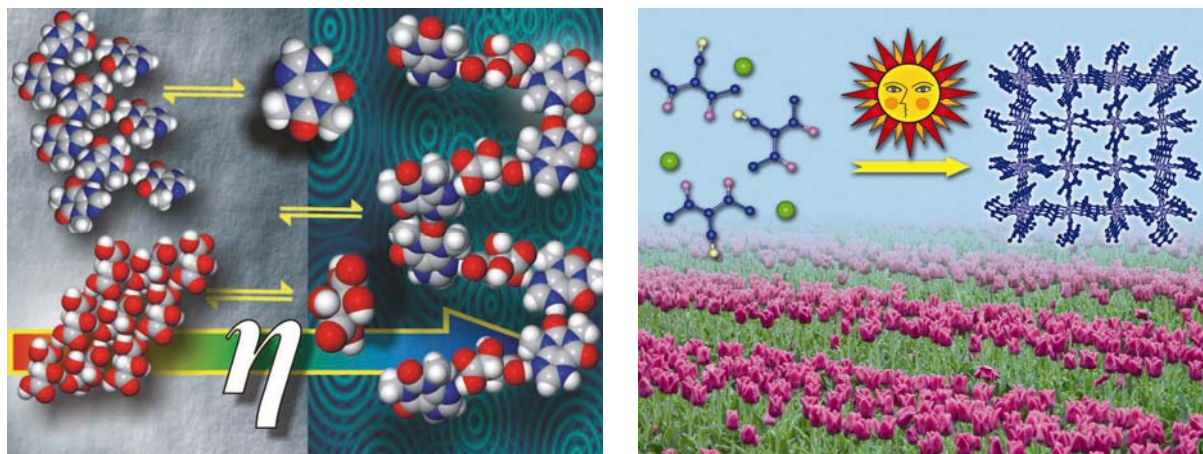
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Mechanochemistry and cocrystals

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Mechanochemistry: the varied applications of mechanical bond-breaking

Gerd Kaupp*

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Mechanochemistry means mechanical breakage of intramolecular bonds by external force and must be differentiated from molecular solid-state chemistry, where contacts between micronized molecular solids are created by the mechanical action for mutual approach of the reacting centers. After an outline of the mechanistic differences, the varied mechanochemistry is discussed. Grinding, milling, shearing, scratching, polishing, and rapid friction (for polymers also cutting, kneading, extruding) provide the mechanical impact for mechanochemistry, while sonication and shock waving for intramolecular bond breaking are generally described as thermal processes. The various types of mechanophysics (e.g., mechanoelectricity, conformational changes, thixotropy, rheopexy, stirring of Newtonian liquids or suspensions, etc.) are not treated here. Mechanochemistry covers solid-state reactions of infinitely covalent crystals, brittle metals, polymers, molecular solids with weak covalent bonds, strong intramolecular bond breakage in shearing Bridgman's anvil or by friction at lubrication of rapidly moving cold contacting surfaces, and single bond breaking or cutting. The diverse wealth of practical applications of mechanochemistry is outlined with typical examples for ceramics, mechanical alloying, hydrogen storage, organic syntheses, waste remediation, leachings, surface plasmas, radical formation, explosives, nanotube formation, nanoparticles grafting, polymer technology, radical initiation, scratch-less polishing, wear protection, lubrication, mechanochromism, nano-dissection, and many more.

1. Introduction

Mechanochemistry is the branch of solid-state chemistry where intramolecular bonds are mechanically broken.¹ We are not dealing here with mechanically induced electron transfers, triboelectricity, and triboluminescence. This is

“mechanoelectricity” as a branch of “mechanophysics”. Also thermal expansion, piezoelectric effects, or compression by pressurizing are to be termed mechanophysics¹ and are therefore not treated here. Furthermore, conformational changes, and changes of intermolecular ligations including hydrogen bonds do not belong to mechanochemistry. For example, thixotropy or rheopexy and related technically important phenomena by stirring/shaking of non-Newtonian

fluids are not to be termed “mechanochemical events” although they require mechanical actions. The same is true for the stirring of Newtonian fluids or suspensions and the mixing or transporting of reactive gases by ventilation. Furthermore, crystallographic phase transitions with minor atomic displacements and no change of the bonding type should be qualified as insufficient chemical change. They belong to “mechanophysics” also when strong bonds are involved in the case of infinitely covalent crystals, because they can also be achieved by hydrostatic pressure. Such phase transitions must be differentiated from solid-state chemical reactions that start with bond breaking. For example, grinding of infinitely covalent hexagonal ZnS (wurtzite) gives cubic ZnS (sphalerite) by shifting atomic positions in the changing lattice (mechanophysics), but the milling of infinitely covalent α -Fe₂O₃ to give Fe₃O₄ and oxygen² belongs to mechanochemistry by initially breaking Fe–O bonds upon mechanical cracking of the crystals, which is followed by the chemical transformation. Also the sole creation of chemical contacts for

University of Oldenburg, Diekweg 15,
D-26188 Edewecht, Germany. E-mail: gerd.
kaupp@uni-oldenburg.de



Gerd Kaupp

Gerd Kaupp received his Diploma and Doctor's degrees from the University of Würzburg in 1962 and 1964, respectively. After staying at Iowa State University, University of Lausanne and University of Freiburg, he received his Habilitation and an Associate Professorship at the University of Freiburg in 1980. He was appointed Full Professor at the University of Oldenburg in 1982. His research interests are in the area of kinetics, mechanisms, heterocycles, photochemistry, supermicroscopy, nanoscratching, waste-free reactions for environmental protection, solid-state chemistry, reactive milling, interactive publishing and new bionics models.

initiating chemically driven reactions between solid molecular reagents is not “mechanochemistry”. For practical and mechanistic reasons the term mechanochemistry must be restricted to breaking of intramolecular bonds directly by an external mechanical action, which is followed by further chemical reactions. Clearly, mechanochemistry means that mechanical energy is used for bond breaking as the first step in chemical transformations. We deal here with the mechanochemistry of infinitely (symmetric and asymmetric) covalent inorganic crystals, metals, polymers, low molecular mass molecules with weak or strong bonds, and single molecules. Milling, grinding, shearing, kneading, stirring, pulling, and cutting does not constitute “mechanochemistry” if the mechanical action does not directly break intramolecular bonds but rather creates contacts of micronized molecular crystallites for solid-state reactions that are chemically driven. This has often not been acknowledged in the literature, which led to severe confusion. Therefore, a critical section 2 dealing with the differentiation of mechanochemistry from molecular solid-state chemistry has become necessary.

2. Molecular solid-state chemistry *versus* mechanochemistry

At solid-state molecular reactions grinding or milling does not mechanically activate the reactants in the absence of weak bonds. Also solid salt reactions are not mechanically activated in the absence of significant charge separation upon cracking. In particular, it is not possible to enforce energetically uphill reactions in these cases. The milling has to create repeated contacts between the micronized reacting crystals for chemically driven reactions, nothing else. This fact has been amply proven by AFM (atomic force microscopy) scans close to the contact edge of reacting molecular crystals in various instances. The occurrence of the chemical reaction without any mechanical impact could be followed by anisotropic molecular migrations up to 1 or 3 mm from the contact edge as detected by AFM. The always-found anisotropic feature formation verifies chemical reaction also in the absence of grinding or

milling.^{3–7} All of these reactions are chemically driven and preparatively used. Exhaustive reviews are available for >1000 solid-state molecular reactions that are waste-free with 100% yield⁸ and for stereoselective ones.⁹ The mechanistic aspects have also been reviewed.^{1,10}

Unfortunately, various authors uncritically claimed “mechanochemistry” or “mechanochemical reaction” when they ground or milled or kneaded strong-bond molecular solids or even liquids. Clearly, one has to differentiate between chemically driven and mechanically initiated reactions. But such distinction is also not followed in reviews on “mechanochemistry” as in ref. 11 where “mechanical activation” is equated with “mechanochemistry” also in the cases of pure mechanophysics and where also chemically driven solid-state reactions are unduly invoked, or even worse in ref. 12 where chemically driven intercrystalline reactions and mechanophysics are integral parts of the undue discussion using the term “organic mechanochemistry”, to name the most recent ones. Only grinding or milling of crystals of molecules with weak bonds can break the weak ones, if their strength is comparable to that of the intermolecular ligations, including hydrogen bridging.

Unfortunately, the lacking differentiation of mechanochemistry and molecular solid-state chemistry in all recent books on “mechanochemistry” has been misleading various authors of original papers to use the terms “mechanochemical” or “mechanochemistry” whenever they used a mortar with pestle or a mill, even if their actions were only micronizing crystals of molecules with strong bonds and creating nanoscopic contacts between crystallites for chemically driven reactions. Undue follow-up claims were then also so called “mechanical activation” or “influence of high pressure” for purely chemically driven reactions. For example, the milling reactions of C₆₀ with solids or even liquids have been misinterpreted with claims of “mechanical activation” due to “high impact” and “very high local pressure” because they seemed to be “mechanochemically” accelerated.¹³ There was however no temperature control, which has been state-of-the-art in reactive milling since at least 1992,^{1,14,15} and there was also no appreciation of the fact that the very insoluble C₆₀ crystals

were cracked by breaking of intermolecular cohesive ligations producing very high surface area for the solid-solid reaction with equally micronized reagent crystallites or with liquids. A fair reactivity comparison for solid-liquid reactions would be the use of pre-milled C₆₀ for the reaction with the liquid at the temperature that was reached in the uncontrolled milling.

In real mechanochemistry mechanical energy is used to initiate decomposition reactions to mostly highly energetic species that induce follow-up reactions of various kinds. Particular mechanical conditions are required if strong bonds of molecules are to be mechanically broken. Shearing under Bridgman’s anvil, or shearing of low molecular mass lubricants under heavy frictional conditions at low to moderate temperatures is most prominent. These molecules must be highly confined so that they cannot escape. In polymers and infinite covalent crystals mechanochemical strong-bond breaking occurs without further confinement, because there is no escape from the impact, and high-energy radicals are obtained.

Mechanochemistry also produces radicals by bond breaking of weak-bond radical initiators, and many explosives. Impacted explosives can explode according to different mechanisms (for example ref. 16). Some typical unstable compounds with weak bonds are peroxides, disulfides, sulfur, *etc.* Only their weak bonds are mechanochemically broken in competition with the cracking of the crystal, when intermolecular ligations of comparable strength are broken. There are limiting cases that clarify the difference between mechanochemistry and molecular solid-state chemistry: if solid diazonium salts are hit with a hammer on an anvil they explode (mechanochemistry); if the same solid diazonium salts are cautiously co-ground with KI (in excess for safety reasons) solid aryl iodides and nitrogen are quantitatively obtained (molecular solid-state chemistry).¹⁷

Mechanic alloying of brittle constituents is another branch of mechanochemistry, when the creation of coordinately unsaturated surfaces by cracking (as compared to the simple removal of passivating surface layers) is essential for the chemical reaction. More pronounced mechanochemistry is obtained with infinitely covalent crystals of elements, oxides, sulfides, and many other ceramic

materials. These produce surface plasma by cracking upon mechanical impact. The surface plasma consists of densely arranged radical centers extending over both fragment surfaces after the sudden breakage of all strong covalent bonds that existed between them prior to the event. It is a state far away from any thermodynamic consideration. People have been using it for thousands of years for igniting fire by hitting natural flint stones and thus mechanically producing sparks by reaction of the plasma with air. More recent applications are the mineralization of every organic material by milling with sand or glass. Ref. 18–20 contain a large number of organics from methane to tetrachloro-dibenzodioxine TCDD that were mineralized by mechanochemical milling with various infinitely covalent solids. In all of these experiments the mechanical impact is decisive and activating. On the other hand, molecular van der-Waals and hydrogen-bonded crystals (with the exception of weak-bond molecules) or salt crystals are not mechanically activated upon ball milling.

The clear differentiation of mechanochemistry from molecular solid-state chemistry upon milling is of uppermost importance for practical synthetic reasons. For example, numerous undue claims and misinterpretations with regard to the term “mechanochemistry” in the literature have been tempting uncritical authors to increase the ball speed beyond an optimal level with so-called high-speed mills²¹ or with planetary mills also for the molecular solid-state reactions. However, high impact makes many mixtures of reactive crystals stuck to the walls of the milling vessel rather than maintaining powders throughout, or it creates sticky clots by local (intermediate) liquefying. If the materials get stuck, real milling ceases and some kind of inefficient kneading starts with the result of extremely long milling times, low yields, and no scalability. Examples of seemingly undue conditions for actually molecular reactions are found in the (unduly termed “mechanochemical”) syntheses of phosphorus yields from solid phosphonium salts and K_2CO_3 with huge milling times of up to 20 h.²² Also the molecular (unduly termed “mechanochemical”) proline catalyzed liquid–solid aldol reaction with huge milling times of up to 36 h (planetary mill; 15 min milling periods

with 5 min pause), or solid–solid reactions with liquefaction up to 36 h, and homogeneous liquid–liquid reactions up to 38 h²³ suffer from the increased impact without temperature control. Some of these are melt reactions with kneading as long as the mixtures are or become honey-like, but the use of a ball mill for homogeneous liquid mixtures of low viscosity is not at all comprehensible. Simply heating such homogeneous liquids to the temperatures that were reached in the planetary mill would have the additional advantage of allowing for scale-up to the kg range or beyond.^{15,24} Solid state ball milling with cooling below eutectic temperatures and without the clotting impact of a planetary mill would have profited from the considerably decreased activation energy in the solid state with short milling times for powdery products.^{1,15} Another undue technique not involving “mechanochemistry” was used for the Heck–Jeffery reaction of aryl iodides with methyl-2-*tert*-butoxycarbonylaminoacrylate, $Pd(OAc)_2$, $NaHCO_3$, HCO_2Na , $n-Bu_4NCl$, and $NaCl$ that gave low yields after 1 h in a planetary mill and involved liquid phases at uncontrolled temperatures.²⁵ It is to be suggested that short pre-milling of the solid components, adding the organics, and heating with stirring will be a versatile alternative with scaling potential. Stoichiometric reactive ball milling of solids with liquids (or involving liquid phases) at controlled temperatures can only be a useful substitute for melt reactions if the properties of the compounds exclude a reliable mixing of the partners in a heated flask. Examples are the quantitative condensation of aldehydes and ketones with wetted 2,4-dinitrophenylhydrazine

(sticky mixture, a few liquid products) or with hydroxylamine hydrochloride (sticky mixtures, a few liquid products). The kneading times in a vibrational ball mill at 20–25 Hz were 10–20 min for the aldehydes and about 30 min for the ketones at 20 K higher temperatures.²⁶

3. Mechanochemistry of crystals with infinite covalent networks or layers or strings

The mechanochemical mechanism

Mankind invented mechanochemistry by creating surface plasmas more than 5000 years ago. By hitting flint against flint (usually natural quartz) in air sparks are produced that ignite some tinder. The crystal lattice of α -quartz (Fig. 1) is built of SiO_4 tetrahedra that are infinitely connected at all corners by strong covalent Si–O–Si bonds in a uniform 3D network. Clearly, if such a crystal is mechanically cracked all new faces exhibit extended extremely reactive surface plasmas of oxygen and silicon radical sites, because all bonds that previously connected the separated surfaces were cleaved by the mechanical impact. This is indicated in Fig. 1 by the residual bond lines of both parts that were moved in the direction of the other diagonal. The results are sparks by rapid chemical saturation of the surfaces with the constituents of air, for example with N_2 and O_2 producing smelly nitrogen oxides. Such reaction of gases with surface radical plasma is not unusual. For example, Si_3N_4 can be synthesized by milling of silicon in N_2 or NH_3 atmospheres.²⁷ Infinite covalent (often asymmetric electron distribution) crystal lattices include infinite strings and sheets.

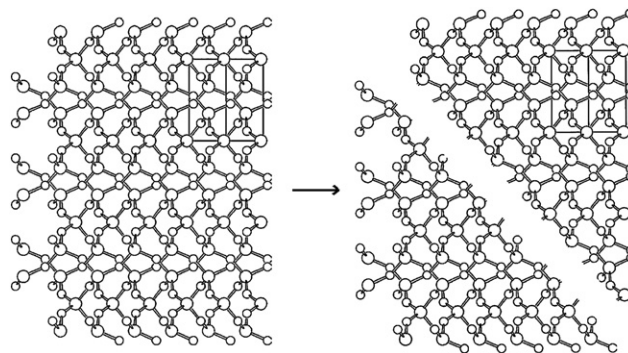
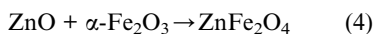
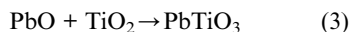
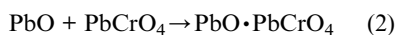
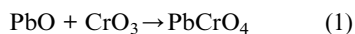


Fig. 1 Crystal packing of α -quartz projected on (1–100) before and after cracking along the diagonal plane, indicating the radical centers on O and Si on both fracture-surfaces (Si: larger circles, O: smaller circles); the projection hides all atoms and bonds that are behind in the z -direction.

Extremely reactive surface plasmas can be used in various ways, even large-scale in industrial ball mills.¹⁵ Very important are cold syntheses of ceramics by co-milling of different infinitely covalent crystals at ambient temperatures. For example, large-scale experiments in an industrial 2 l horizontal rotary ball mill (Simoloyer®) have been performed



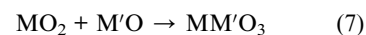
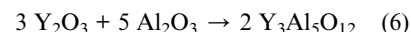
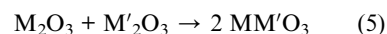
The high melting ceramics are accessible by the mechanochemical reactive milling of stoichiometric mixtures of the very high melting oxides close to room temperature, because the extended surface plasmas react with other surface plasmas or with unbroken surfaces to finally form the most stable ceramic possible. For example, PbO (litharge or massicot) crystallizes in layered structures, and CrO₃ or TiO₂ (rutile or anatase) exhibit 3D crystal lattices. PbO and CrO₃ form chrome yellow PbCrO₄ (crocoite, *P2₁/n*, infinitely 3D-connected) when milled at room temperature (1), which can be converted further to chrome red (PbO·PbCrO₄, phoenicochroite) by milling with the additional quantity of lead oxide (2).^{15,19} Metal–oxygen bonds are by necessity mechanically broken if the oxide crystals with infinite 3D-network or infinite covalent layers, are mechanically cracked. Also ferroelectrics such as lead titanate PbTiO₃ (macedonite, *P4mm*) with high dielectric constants (PLZT ceramics) (3) and ferrites such as zinc ferrite ZnFe₂O₄ (franklinite, Zn-spinel, *Fd3m*) (4)²⁸ have been prepared by high kinetic milling with the Simoloyer®.^{15,19} Typical conditions were 2 kg of steel balls with 5 mm diameter for a 2 l mill at 1200 rpm at room temperature and 200 g of material. The milling times were up to two hours, because the conversion rate dropped down if the particles became so small that the chances for being broken decreased. The highly disordered zinc ferrite is an improved catalyst that is widely used in industry also for the desulfurization of hot coal gases, or as a ferrite material, or as a heat resistant

yellow pigment. The large-scale production in the semi-continuous Simoloyer® mill provided this valuable material in aggregated form of nanoparticles much cheaper than the high temperature production at 700–900 °C or 1000–1100 °C followed by milling.

Several related mechanochemical syntheses of ceramics at low temperatures have been executed primarily in planetary ball mills on a small scale. These reactions have been rightfully termed “mechanochemical” but without appreciation of the mechanically generated surface plasmas, despite their inevitability.^{1,15} When rather long milling times were reported, it might be suspected that the materials adhered to the walls of the milling beaker due to excessive mechanical impact in the planetary mills. It should however be tried to maintain loose powder and much higher collision numbers as achieved in the technical rotary mill with numerous smaller balls. Almost certainly, these syntheses could be largely improved with the available industrial rotor ball mills on a large scale. These syntheses cover various types, from where typical examples are selected.

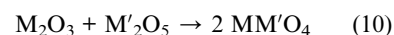
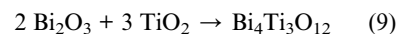
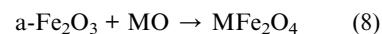
Milling of further 3D-covalent structures

Sesquioxides of different metals exhibit 3D-covalent networks. They form important perovskite-type oxides by co-milling stoichiometric mixtures close to room temperature (5). The crystal structures of the components can be different. An early report reacted $\alpha\text{-Fe}_2\text{O}_3$ (corundum-type) with Bi₂O₃.²⁹ M could also be Fe and Cr (corundum type), when M' was Sm (Sc₂O₃ type), or La, Nd, and Pr (layered La₂O₃-type) (5).^{30,31} Very potent surface plasmas upon cracking the corundum structures should guarantee efficient reaction with the infinite La₂O₃ layers that are also mechanically cracked and the radicals at the end face of the broken sheets can then also react with nanosized hematite. Similarly, Mn₂O₃³² or Al₂O₃³³ and La₂O₃ formed the corresponding 1 : 1 mixed oxides (5). A different ratio of the sesquioxides is required if garnets shall be formed. Thus, the laser material YAG was obtained in amorphous form upon milling of yttrium oxide (Sc₂O₃ type) with alumina (6).³⁴



Another technique for obtaining MM'O₃ ceramics is the milling of oxides of two- and four-valent metals (7). For example, this has been achieved with the 3D infinite TiO₂ (rutile or anatase) and CaO,³⁵ BaO (4 h),³⁶ and PbO,³⁷ or with SnO₂ and ZnO,³⁸ or with MnO₂ and SrO.³⁹

Infinite oxides of three- and two-valent metals provide ferrites (8). These were obtained from hematite and for example ZnO^{15,19,40} or MgO,⁴¹ CaO,⁴² NiO (50 h),⁴³ and MnO (20 h).⁴⁴



Continued milling has mechanochemically combined the infinite oxides of three- and four-valent metals. The important “ferrite” Bi₄Ti₃O₁₂ was formed in a planetary ball mill at a 2 : 3 ratio (9).⁴⁵ We note here also the silicate formation by milling of SiO₂ and La₂O₃ for 9 and 18 h.⁴⁶ Furthermore, continued cracking in a mill has mechanochemically combined the infinite oxides of three- and five-valent metals (10). For example M was La, In, Bi, or Cr and M' was V. Also the pentoxides P₂O₅, Sb₂O₅, Nb₂O₅ and Ta₂O₅ have been successfully reacted with In₂O₃ (10).⁴⁷ All of that is in full support of the surface plasma mechanism (Fig. 1). Such plasma formation must also be at work in the small-scale formation of $\alpha\text{-Al}_2\text{O}_3/\text{M}$ composites that were obtained if Al metal was milled with the metal oxides M_xO_y, of M = Fe, V, Cr, Mn, Co, Ni, Cu, Zn, Nb, Mo, W, Si in the proper ratio.⁴⁸ Another redox reaction occurred upon large-scale milling of Ag₂O with Ag₃Sn to give SnO₂ and Ag as a highly dispersed composite electrical contact material.^{49,50} It is not clear if that is only in part mechanochemistry, because Ag₃Sn is very ductile, but Ag₂O has an infinite cuprite structure (Ag–O distances: 2.0438 Å) that might also be cracked after penetration into the ductile intermetallic phase. An AFM study^{3–7} would be helpful in this respect. The plasma formation upon milling of

infinite oxides can also be used for reaction with salts. For example, the catalytic activity of SrTiO₃ for NO-removal has been improved by “fluorine-doping” *via* milling with SrF₂ for 1 h.⁵¹

No “mechanochemistry” should be claimed if two different salts form a complex salt upon co-milling, as no covalent bonds are mechanically broken and salts prefer to cleave without generating extended charge separations. This has not been appreciated in the syntheses of the complex salts (NH₄)₃GaF₆, KZnF₃, NaLaF₄ (4 h),⁵² but was fully pointed out when Na_n[Cu(CN)_{n+1}] (*n* = 1–3) were synthesized depending on the molar ratio of NaCN and CuCN by large-scale milling, each in 30 min.¹⁵ The salt reactions are chemically driven. Milling creates the contacts. Also the oxidation of sodium nitrite with NO₂ gas to give sodium nitrate and NO gas, where the milling removed the passivating layers from the surface, is not mechanochemistry.¹⁵ It is just not right that every reactive milling or grinding is “mechanochemistry”.

Scratch-less polishing of 3D infinite covalent materials and nanoscratching

Mechanochemistry of infinitely covalent ceramics is not restricted to grinding and milling. It covers also polishing and heavy load friction (section 9, below). There is a high need for scratch-less polishing of hard materials such as silicon nitride, sapphire, silicon single crystals, SiC, ZrO₂, *etc.* This can be mechanochemically achieved by polishing with softer abrasive materials exhibiting an infinite covalent structure to produce precision ceramics. The polished surfaces can then be analyzed using Auger spectroscopy.⁵³ For example, fast rotating Si₃N₄ discs were polished with softer fixed Cr₂O₃ disks to improve peak to valley heights from 170 to 40 nm or from 700 to 50 nm.⁵⁴ It appears that asperities on the Si₃N₄ surface scratched the Cr₂O₃ surface with formation of surface plasma on the abraded Cr₂O₃ particles that reacted with the harder Si₃N₄ surface to produce chemically transformed layers ready for abrasion by Cr₂O₃. Support for our mechanistic interpretation can be deduced from ref. 55 where Si₃N₄ was polished with Fe₂O₃ and Fe₃O₄ at removal rates up to 1.6 μm h⁻¹ using the

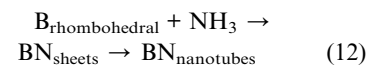
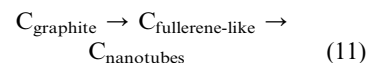
softer abrasives on a linen plastic lap. The final peak-to-valley roughness of the scratch-free polished surfaces was <20 nm. Importantly, Auger spectroscopy of these surfaces revealed a thin layer (≤10 nm) containing a silicon oxynitride (a possibility might be sinoite: Si₂N₂O), iron, and some carbon. This is good support for our mechanochemical view of such polishing. Also polishing with pads from various organic polymers led to scratch-less surfaces.⁵⁶ Apparently, the free radicals formed by abrasion reacted with the substrate surface to give more easily removable compounds as above. Other so-called “mechanochemical polishing” techniques with softer particles that were applied to easily oxidized or slightly soluble surfaces used additional liquid oxidizing agents such as peroxides or acids. However, these techniques are at best partly mechanochemical.

A modern surface scratching technique that is related to polishing actions is nanoindentation and nanoscratching. When it was applied to infinitely covalent materials or polymers mechanically induced bond cleavages were achieved with the consequence of phase transitions under the local pressure. This severely influenced the measured nanohardness and elasticity modulus values.⁵⁷

Milling of layered structures

Graphite has an infinite structure of layered aromatic bonds, which enables mechanochemistry by milling. Numerous strong bonds are broken upon disruption of the layers producing free valences along the fresh borders. This opens the way for formation of the interconnected fullerene-like ball structures of turbostratic graphite.⁵⁸ It should rely on the connection of new bonds between the free valence centers of small disrupted particles, leaving nanopores. Annealing of turbostratic graphite at 1400 °C provided carbon nanotubes (11).⁵⁹ A direct fabrication of carbon nanotubes with diameters of 10–300 nm and lengths up to several micrometres by ball milling of graphite was also reported.⁶⁰ Curling up to nanotubes upon breakage of infinite layers might be a more general phenomenon. For example long milling of hexagonal BN sheets (that are formed by milling of boron in an ammonia atmosphere) produced a high density of

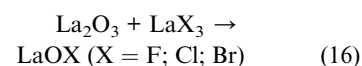
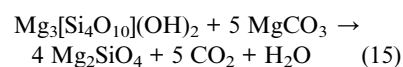
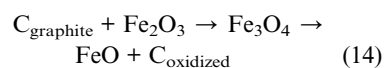
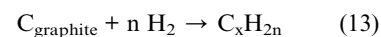
nanotube nuclei, that grew to cylindrical and bamboo-type BN nanotubes upon subsequent heat treatment at 1200 °C (12).^{61,62}



Surprisingly, MoS₂ and WS₂ nanotubes have not yet been reported to occur from milling of the layered disulfides, even though such nanotubes were obtained by thermal decomposition of ball-milled MoS₃ and WS₃, or (NH₄)₂MoS₄ and (NH₄)₂WS₄ in H₂/CH₄/thiophene atmosphere at 300–450 °C.⁶³ However milled MoS₂ exhibits catalytic activity in hydrogenations.⁶⁴

If carbon nanotubes were milled for 15 min, they broke and also formed onion-like particles. Milling for 60 min produced amorphous carbon.⁶⁵ The breaking of multiwalled carbon nanotubes was used for functionalizing under reactive gas atmosphere such as CO, COCl₂, Cl₂, NH₃, or CH₃SH in a ball mill, when the tube lengths decreased to 200–300 nm and the inner pore of the nanotubes became accessible.⁶⁶ It was also possible to wrap multi- and single-walled carbon nanotubes with DNA, when the co-milling cut the tubes into shorter lengths of 0.5–3.0 or 0.25–1.0 μm, and a high aqueous solubility ensued.⁶⁷ Clearly, the edges of the breakages must have provided the unsaturation for the binding of the DNA.

If milling of graphite was performed under H₂ atmosphere, amorphization occurred⁶⁸ obviously by saturation of the fresh reactive borders with hydrogen (13). Planetary ball milling (room temperature, 80 and 120 h) of graphite with hematite (α-Fe₂O₃) gave solid-state reduction to magnetite (Fe₃O₄) and wustite (FeO) (14).⁶⁹ Talc is an example of an infinitely

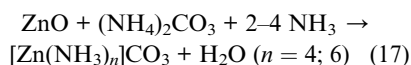


covalent layered structure. It reacted with magnesium carbonate to give forsterite upon co-milling (15).⁷⁰ Radical formation by mechanical breakage of layered La_2O_3 has also been used for reaction with salts to produce lanthanum oxyhalogenides (16).⁷¹

4. Use of mechanochemical surface plasma for leaching

The comminution of metal oxides and various minerals by dry milling enormously increases the surface of aggregated nanoparticles that immediately saturate their surface plasma. The crystal lattices are largely distorted and the wet leaching is facilitated. For example milled electric arc furnace EAF dust can be leached with 2N HCl at room temperature for dissolving ZnO, partly Fe_2O_3 and Fe_3O_4 , PbO, CdO, CuO, and further minor oxides, but not significantly the valuable component zinc ferrite ZnFe_2O_4 , which can be used industrially.⁷² It is however also possible to completely dissolve such comminuted zinc ferrite in constant boiling 20% HCl at 110 °C in 30 min.⁷² Similarly, yttrium containing fluorescent powders were dry milled to improve the extraction yield.⁷³ This technique was extended for the recovery of rare earths from fluorescent powders in waste lamps, or of indium from indium tin oxide ITO scrap, followed by leaching with mild acid solutions at room temperature.⁷³ The presence of $\alpha\text{-Al}_2\text{O}_3$ was helpful for the milling. Another advanced waste processing is the recovery of Mo, V, and Ni sulfides from catalysts in oil refineries by milling with CaO, MnO and Na_2CO_3 to transform them into leachable molybdates and vanadates.⁷⁴ Also previous dry milling facilitated the acid leaching of magnesium from garnierite or serpentine ores.⁷⁵

Wet milling of surface plasma producing solids is more efficient, because water immediately reacts with formation of hydroxides. This allows also alkaline leaching of EAF dust in ammonia with ammonium carbonate (17). Zinc, lead, and cadmium oxides are leached, but zinc ferrite and most of the iron oxides remain insoluble. ZnFe_2O_4 can be isolated after acid treatment, which removes the iron oxides.⁷⁶ Also the Bayer process is improved by

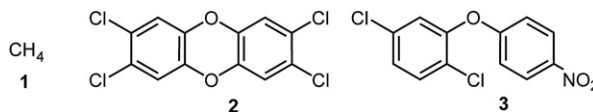


alkaline wet-milling of bauxite for leaching of gibbsite $\{\text{Al}(\text{OH})_3\}$ as a starting material for the aluminum production.⁷⁷ Many further applications are at work in hydrometallurgy, and further ones may be envisaged since large efficient industrial rotor mills are available.

5. Use of mechanochemical surface plasma for reactions with organics

An interesting application of the mechanically generated surface plasma of infinitely covalent materials (tribomaterials) is their use for decontamination of all kinds of organic materials from methane **1** to the most poisonous environmental threats by complete mineralizing. Surface plasma formers include oxides (quartz sand, glass with amorphous SiO_2 , CaO, MgO, TiO_2 , Al_2O_3 , Fe_2O_3 , Fe_3O_4 , ZrO_2 , B_2O_3 , *etc.*), sulfides (FeS , FeS_2 , ZnS, *etc.*), nitrides (BN , Si_3N_4 , *etc.*), carbides (B_4C_3 , SiC, WC, *etc.*), silicides (FeSi_2 , TiSi_2 , *etc.*), infinitely covalent elements (B, C, Si, *etc.*), ceramics, and composites (granite, quartz porphyries, enamel, *etc.*). Such surface plasma (compare Fig. 1) eagerly tends to become immediately saturated by reaction with admixed organic compounds. High kinetic co-milling with excess tribomaterial completely mineralized the admixed organic residues including environmental poisons such as PCBs, HCHs, DDT, polychlorinated dioxins (including TCDD **2**) or furans, nitrofen **3**, anti-fouling tin organics, *etc.*^{15,19,78} The end products were carbon (graphite), water and HCl. The starting tribomaterials (*e.g.* sand) may have diameters from 10 μm up to about 1 mm. The technique becomes less efficient if the sizes drop down to the nanoscale upon milling, because the chances for being cracked decrease. For technical application⁷⁸ recycling by melting of the final powder and crushing of the cooled material to sizes that can be adapted by the mill is most easily achieved

with glass wastes of every quality (windows glass, Pyrex, Duran, Solidex, *etc.*). The carbon from the previous use is burned away. For example 200 g of dry sand were milled with methane gas **1** (avoid the presence of oxygen for safety reasons!) to produce graphite and water by reaction with the plasma of free $\equiv\text{Si}^\cdot$ and $\cdot\text{O-Si}\equiv$ surface radicals. Correspondingly, 0.21 g of tetrachlorodibenzodioxin **2** with 0.30 g congeners and 0.2 g KCl, or 0.8 g pure nitrofen **3** was completely mineralized with 200 g of Duran glass fragments within 30 min in the 2 l Simoloyer® rotor mill with 2 kg steel balls (CR6) at 1300 rpm, when the temperature rose to 40–60 °C, and the energy consumption was 0.325 kWh. No trace of residual poisonous material could be detected by modern mass spectrometry. Organic poisons that occur adsorbed to fly ashes, graphite, or other supports were also completely mineralized.⁷⁸ XPS measurements on the final powders exhibited the peaks of graphite.⁷⁸ This is a benign closed cycle low temperature decontamination process for safe and complete removal of the hazards one has with non-disposable organic wastes. The surface plasma mechanism did not work out with the interesting case of sodalite $\text{Na}_8[\text{Si}_6\text{Al}_6\text{O}_{24}]\text{Cl}_2$. It exhibits an infinite 3D-frame of SiO_4 and AlO_4 tetragons, but does not form effective plasma upon cracking, because the lattice-NaCl immediately saturates the surface. Therefore, *o*-dichlorobenzene remained unaffected upon co-milling with sodalite. The plasma mechanism (Fig. 1) is convincingly verified by the failure of such mineralization of organics if high-melting salts such as NaCl, CaF_2 , BaSO_4 , apatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH},\text{F})_2$, ZrSiO_4 , other island silicates, *etc.* are milled in their presence, because salt structures cannot form surface plasmas upon milling. Our plasma techniques are easily executed and most benign. Another approach tried reductive removal of halogen from polyhalogenated aromatics by milling with sea sand, calcium oxide, large excesses of metallic sodium or magnesium, and ethanol in planetary ball mills (typically



5 h) or eccentric swing-mills (typically 90 min) to form aromatic hydrocarbons, strongly basic wastes, and hydrogen that forms explosive mixtures with air.⁷⁹ Further approaches for the decomposition of halogenated aromatics with formation of hydrocarbons, phenols, and char used planetary mills with incomplete amounts of tribomaterial. 3-Chlorobiphenyl (CBP), 1,2,3-trichlorobenzene, and chlorine containing aromatic polyamide (aramide) gave almost complete dechlorination during about 6 h milling with CaO, CaCl₂, CaCO₃ and amorphous carbon were found among the still poisonous aromatic decomposition products.⁸⁰ The aramide gave rupture of covalent C–C, C–Cl, C–N, and C–H bonds.⁸⁰ Addition of quartz increased the rate of decomposition of CBP. This was interpreted as a “breakdown of the agglomerates”.⁸¹ Similarly, milling of polyvinyl chloride PVC powder with CaO, Fe₂O₃, SiO₂, or Al₂O₃ dechlorinated and reduced the molecular mass by chain breaking and formation of C=C double bonds.⁸² The same results ensued by milling PVC with oyster shells.⁸³ When polytetrafluoroethene PTFE was milled with La₂O₃ (≥4 h) amorphous carbon, LaOF, and La(CO₃)F were obtained.⁸⁴

An application of mechanochemistry in catalysis is the improvement of the photocatalytic ability for the nitrogen monoxide destruction with respect to pure SrTiO₃ when it was “nitrogen doped” by ball milling with urea or hexamethylenetetramine, followed by calcination at 400 °C.⁸⁵ We note that strontium titanate crystals have an infinite 3D network of Ti–O bonds (*Pm3m*; Ti–O bond length 1.953 Å) and are therefore able to form the necessary surface plasma upon milling.

The surface plasma formation by cracking SiO₂ or Al₂O₃ is also evident from the polymerization initiation of ethene by ball milling. Polyethene PE grafted to SiO₂ or Al₂O₃, and homopolyethene was obtained.⁸⁶ Corresponding results were obtained if quartz and polymers were co-milled. For example, filler qualities were improved by mechanochemical grafting of SiO₂ with polyacrylonitrile PAN⁸⁷ or polypropene PP.⁸⁸ Also mica, kaolin, and volcanic tuff were grafted by milling with acrylonitrile, methyl methacrylate, and vinyl chloride.⁸⁹ Such grafting to ceramics modified silica

nanoparticles by co-milling with N-vinylpyrrolidone⁹⁰ or with ethene–propene block copolymer.⁹¹ Various acrylamides and acrylic arylesters were polymerized by initiation with milled quartz, quartz glass, feldspar, or talc. The reactions started at the surface radical centers, but the conversions were rather low (2–8%) at 30 h milling in Si₃N₄ beaker and balls.⁹² The claimed initiations by limestone and marble must, however, rely on non-salt impurities. Clearly, initiations by mechanical bond breaking are very important techniques.

6. Mechanochemistry of semimetals and metals

Typical semimetals (As, B, Bi, Ge, Po, Sb, Se, Si, Te) exhibit non-metallic polymorphs with covalent bonding. They are able to form intermetallic compounds, such as the minerals allemontite (SbAs) or calaverite (AuTe₂). If comilling of the constituents formed these it would be genuine mechanochemistry. Actually, comilling of As and Mn at room temperature provided MnAs,⁹³ or germanium was alloyed with silicon at optimized planetary ball milling.⁹⁴ Silicon also formed silicon carbides by milling with graphite (40 h)⁹⁵ and with numerous metals (for example Mg, Ti, Fe, Co, Ni, Cr, Mo, Pd). Various distinct phases of iron silicides were synthesized (Fe₁₄Si, Fe₉Si, Fe_{6.5}Si, Fe₄Si, Fe₃Si) for the study of their lattice parameters and magnetic properties.⁹⁶ TiSi was obtained as amorphous or intermetallic phases, depending on the co-milling procedure of the components.⁹⁷ All four equilibrium phases in the Cr–Si system (CrSi, CrSi₂, Cr₅Si₃, Cr₃Si) could be obtained and these formed stepwise.⁹⁸ Also the components B, Si, Fe, Cu, and Nb could be comilled in the right proportion to obtain magnetically soft nanocrystalline finemet alloy (Fe_{73.5}Cu₁Nb₃Si_{13.5}B₉) powder, which was compared with milled ingot material from the induction melting synthesis.⁹⁹ Thermoelectric materials β-Zn₄Sb₃¹⁰⁰ and Sb₂Te₃¹⁰¹ were prepared by ball milling of the elemental components in the correct ratio. The powders could be sintered for making use of them. Various further metal/semimetal combinations have been exhaustively studied. In all cases, the radical surface plasma of the semimetal is highly reactive for the fresh metal

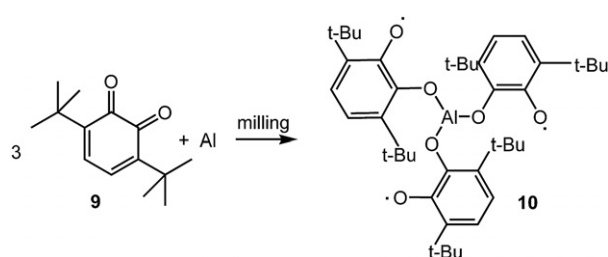
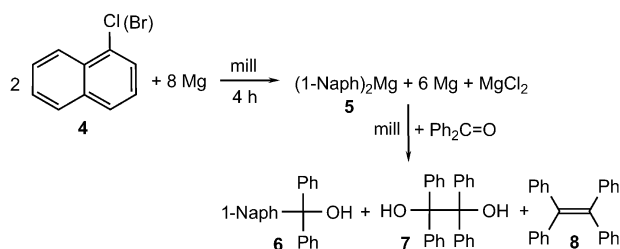
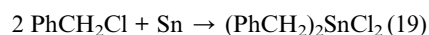
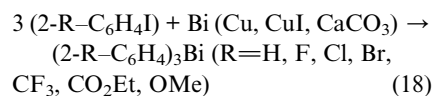
surfaces, and the intermediates continue with the reaction upon ongoing milling.

Metals exhibit particular metal bonds with easily movable electrons in conduction bands. Therefore, radical plasma according to Fig. 1 cannot form upon cracking of brittle metals. However, all atoms on a cracked metal surface miss their previous neighbor atoms and are therefore highly reactive. Usually this leads to oxide or hydroxide layers in air and sometimes to violent pyrophoric oxidation with enormous heat production of milled metals. Such oxidation of metals can also be achieved by comilling with metal oxides and there are numerous examples for that (for example ref. 48 in section 3). Similar to Si₃N₄ formation²⁷ the reactivity of fresh metal surfaces can also be used to fabricate metal nitrides, such as MoN₂, TaN, VN, or TiN, when the corresponding metals are ball-milled in an NH₃ atmosphere.¹⁰² Nitriding by milling of Ti and Zr,¹⁰³ Fe, Nb, Hf, or of various alloys in nitrogen atmosphere was also possible. It is therefore very clear that mechanical alloying of brittle metals profits from the increased surface reactivity. On the other hand ductile or liquid metals may alloy by a non-mechanochemical kneading type mechanism. An outline of this vast field including all phases and composites is out of reach for the page limitations of this article. More recent books are available on diverse aspects of mechanical alloying.^{104,105}

Direct reactions of metals for reductions or formation of metal alkyls or metal aryls may require removal of the passivating oxide/hydroxide surface layer. This can be achieved by short milling of the metal in presence of the organic reagent, but it should not be termed mechanochemistry if the reaction proceeds without milling after such trivial depassivation. For example, the exothermic syntheses of aluminum alkyls from aluminum and alkyl halides in the absence of solvents belong here, even though initial milling may largely decrease the induction period. Milling also decreases induction periods of exothermic syntheses of Grignard reagents from magnesium and alkyl or aryl halides. This has industrial importance for the milling in THF solution with Mg.¹⁰⁶ Decrease of the particles was negligible, and creation of fresh metal surface did not appear essential. The

claimed decrease in activation energy of about 5 kcal mol⁻¹ (for exothermic reactions that must be cooled to stay close to room temperature) should probably be attributed to higher turbulence by the milling, but not to “mechanochemistry”. Ultrasonic acceleration of Grignard reagent synthesis in liquids was also reported.¹⁰⁷ The problems with solventless production of Grignard reagents and reactions have been outlined in ref. 108. A 4 : 1 molar ratio of Mg to 1-chloro- or 1-bromonaphthalene **4** was necessary to obtain a solid product after 2–4 h milling. It contained the stable Grignard reagents (probably **5**) in good yields mixed with pyrophoric Mg of high reactivity. Addition of ketones (e.g. benzophenone) and continued milling (20 min) gave therefore not only Grignard reaction to the tertiary alcohol **6** but also McMurry reaction to the “dimeric” pinacol **7** and the alkene **8**, mechanochemical types of reaction, because fresh surface of milled magnesium was essential.

Bismuthanes are not easily obtained in solution reactions. Continuous milling for creating fresh reactive excessive metal surface (mechanochemistry) and catalysis is required for the reaction of Bi with aryl iodides. Bismuth shots (1 mm), CaCO₃, Cu, CuI, and *ortho*-substituted iodobenzenes in the molar ratio of 14 : 0.7 : 2 : 1.4 : 1 were milled for 12 h to obtain tris(2-*R*-aryl)bismuthane in moderate to good yields (**18**).¹⁰⁹ It is highly probable that the reaction proceeded *via* initial arylcopper species followed by ligand exchange with the bismuth atoms on the freshly cleaved surface. More easily, tin and benzyl chloride was milled for 3 h to produce dibenzyl dichlorostannane (**19**).¹¹⁰



The fresh surfaces of milled bismuth or lead are able to deoxygenate nitrobenzenes. The less reactive bismuth gave azoxy benzenes but the more reactive lead gave azobenzenes by milling for 90 min as dark pasty solids for extraction and workup.¹¹¹ Numerous related reactions exist, but it is always to be differentiated if only removals of passivating films or creation of fresh surfaces by mechanical crystal cracking is required.

Reduction of orthoquinones by freshly cleaved metals provided di- or triradical metal complexes. For example, when Al, Ga, Cr, Mo, or W were milled with 3,6-di-*tert*-butyl-orthoquinone **9** the triradical **10** was formed and fully analyzed by ESR and ENDOR spectroscopy.¹¹² Cd, Zn, Sn, and other divalent metals provided the corresponding diradicals.

An important synthesis for hydrogen storage is the milling of Be and Li with H₂ to obtain BeLiH₃ or BeLi₃H₅ with high reversible storage capacity for hydrogen.¹¹³ Again, these reactions are mechanochemical, as the mechanical breaking of metallic bonds must precede.

7. Mechanochemistry with polymers

Creating powders of polymers usually requires stiffening by cooling to low temperatures. Both linear or crosslinked polymers are easily transformed to “mechanochemicals” by milling, shearing, scratching, cutting, or extruding. These have been repeatedly detected by ESR spectroscopy, for example with ball-milled polypropylene PP¹¹⁴ and many others.

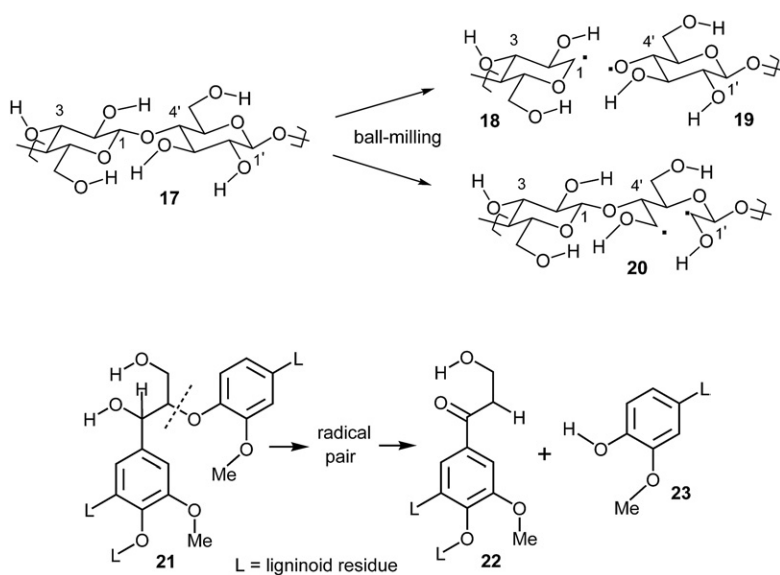
The radicals formed by mechanical breaking of chains or networks undergo the usual free-radical reactions: recombination, disproportionation (to alkene and alkane), addition, and hydrogen abstraction. Cross-linking of vinylic polymers occurs with the radical after hydrogen abstraction and by addition to the alkene from disproportionation, but these “products” are also involved in secondary mechanical bond breaking. Overall the molecular mass is decreasing. Clearly, escape of the polymer chains from impacting mechanical tools is not possible upon milling, grinding, shearing, nano-indentation, or nanoscratching. Strong bonds break mechanochemically with formation of polymer radicals and decrease of chain lengths. Some of the radicals usually survive in the polymer matrix for ESR spectroscopic detection and identification even at room temperature or better at 77 K. Furthermore, the radicals can be trapped by radical scavengers, or they may be used for starting radical chain reactions. The most prominent application of the latter type is the induction of vinylic polymerization of appropriate monomers. The mechanochemical breakdown of all kinds of polymers is long known and we can only cite here some particularly important examples.

Radical polymerizations were initiated when PE or PTFE were milled in the presence of ethene. Such polymerization started from the macroradical centers.¹¹⁵ Similarly, block and graft polymers were obtained by milling of PAN with vinyl chloride or 1,3-butadiene,¹¹⁶ of poly(methyl methacrylate) PMMA with vinyl chloride,¹¹⁷ of poly(ethylene terephthalate) PET with acrylic acid,¹¹⁸ or of polybutadiene rubber with maleic anhydride,¹¹⁹ to name a few. It is, of course, also possible to generate block polymers by co-milling of different homopolymers such as PVC and PMMA,¹²⁰ because macroradicals are able to combine. Too

long milling decreases the molecular masses of all polymers.

A particular situation arises with polymers that contain C=C double bonds in the main chain or in side chains, because they will cross-link upon milling by addition of the macroradicals to the double bonds. Most important is the mastication of rubber by shearing between rollers, in kneaders, or in extruders. Low (roughly room temperature) and high temperature (up to about 200 °C) mastication under oxygen, air, or inert gases provides different results with natural or vulcanized rubbers in the presence or absence of fillers, salts, activators, or radical traps. Large chains are broken and the macroradicals have been trapped with N-oxyl radicals,¹²¹ or they react in various ways. The formula scheme depicts a cross-linking of linear *cis*-polyisoprene **11** by cleavage to **12** that gives **13** and **14** for further radical reactions or competitively disproportionation to give, for example, **15** and **16**. Overall, the molecular mass decreases despite cross-linking upon longer mechanical treatment. All of that influences the plasticity, the Mooney viscosity, and the gelation. For example, extrusion of natural rubber, or isobutylene rubber in the twin-screw counter rotating extruder produces masticated rubber with defined molecular mass by varying shear rate and mastication time.¹²² Natural polyisoprene rubber with bimodal mass distribution stagnated on prolonged high-temperature mastication due to increases in the quantity of short chains.¹²³ The decrease of mastication efficiency of Hevea rubber with increasing temperature (80–115 °C) was due to cross-link formation, similar to that of hardening during storage.¹²⁴

Mechanical treatment by repeated cracking action to cellulose **17** is of uppermost importance in pulp and paper industry. The fiber breakdown is well



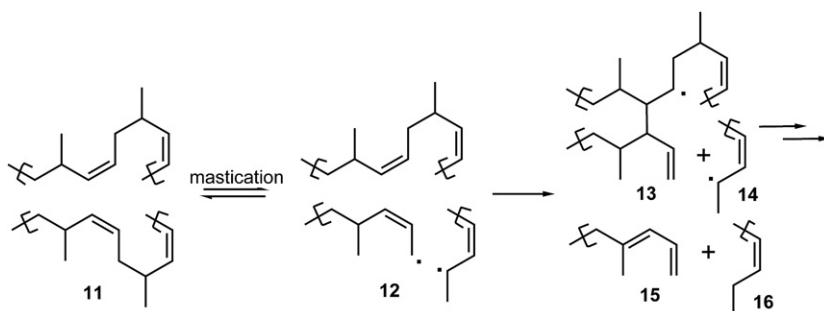
known since 1921¹²⁵ and many papers on mechanical degradation of cellulosic materials have appeared since then, the degradation being reliably detected by viscosity measurements. Also ball milling at room temperature and at 77 K was studied. Early ESR measurements definitely proved the chain cleavages into various radicals as the first step.¹²⁶ Three types of radicals were detected at 77 K and at room temperature. The alkoxy **19** and carbon radicals **18** derived from cleavages at the C1–O–C4'-positions (glycosidic bond) and further carbon radicals **20** occurred by cleavage at the C2–C3 positions of the monomer units. Some of the carbon radicals reacted with spurious or added oxygen to form peroxy radicals. The disproportionation of the selected radicals gives the 2-ketone and the hydroxyl endgroups of the fragments. If methylmethacrylate (MMA) was added, its vinylic polymerization was initiated by the mechanoradicals and propagating radicals of oligo-MMA could be observed by ESR. A high degree of grafting with MMA was found when

co-milling with cotton cellulose,¹²⁷ which also verifies the production of cellulose mechanoradicals.

Mechanical pulping of wood also produces radicals by bond-cleavages of highly polymerized lignins **21**. Phenoxy- and alkyl radicals are produced from lignin **21** by mechanical bond cleavage. The radical pair can disproportionate to give **22** and **23**, or added radical scavengers including oxygen may scavenge the primary radicals. Also the adjacent benzylic C–C bonds are mechanically broken. If radical traps such as phenyl-*N*-t-butylnitron and others scavenge the radicals, the brightness stability is improved. This is highly important in the process of paper production for fighting the light-induced yellowing of bleached high quality paper by suppressing the production of leucochromophores and chromophores. For example, an unbleached or H₂O₂-bleached softwood pulp was milled in the presence of the scavenger and handsheets were subsequently prepared. The brightness was increased and the light-induced discoloration decreased.¹²⁸

8. Mechanochemistry of weak covalent bonds

Radicals are also obtained by mechanical cleavage of weak covalent bonds in low molecular mass molecules. This occurs in competition with the separation of intermolecular ligations (including hydrogen bonds) of the molecular crystals by the milling. Crystalline (non explosive) sulfur



S₈ causes rapid mechanochemical corrosion to various metals upon ball milling due to its weak bonds. The milling of sulfur with copper quantitatively and rapidly produces Cu₂S (20) or CuS (21) depending on the stoichiometric ratio. The corresponding reaction with iron was not completely specific (22).¹⁹ Such large-scale millings should not be performed with steel balls, but the stellite housing and hard-metal rotor were sufficiently resistant when ZrO₂ balls were used. 200 g stoichiometric batches were successfully performed.¹⁹ The pyrite or marcasite (FeS₂) 3D-structures also contain weak S–S–bonds that lead to similar corrosion of iron and steel upon mechanochemical milling to give FeS (23).



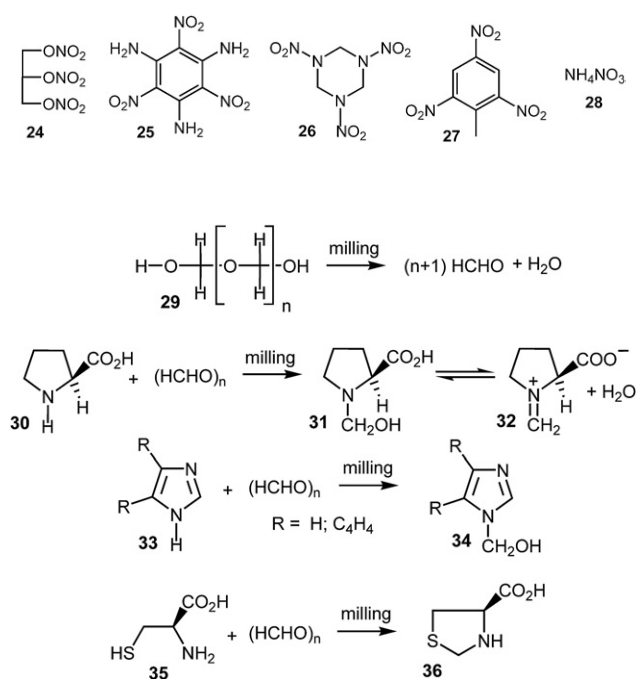
The S₈- and pyrite/marcasite-reactions require mechanochemical S–S bond cleavages by the milling prior to the chemical reaction. These mostly waste-free low-temperature syntheses are useful and many applications of sulfur and pyrite for the synthesis of metal sulfides or organic solid-state reactions (cross-linking, thiiranes, *etc.*) might be envisaged. Clearly, weak O–O–bonds of solid peroxy compounds can also be mechanically broken, but stoichiometric runs of these and other shock-sensitive explosives are risky, despite the very high balls to crystals mass ratios. Many common radical starters, for example solid aliphatic azo compounds, peroxides, hydroperoxides, peresters, *etc.* can be mechanochemically activated for the initiation of radical chain reactions.

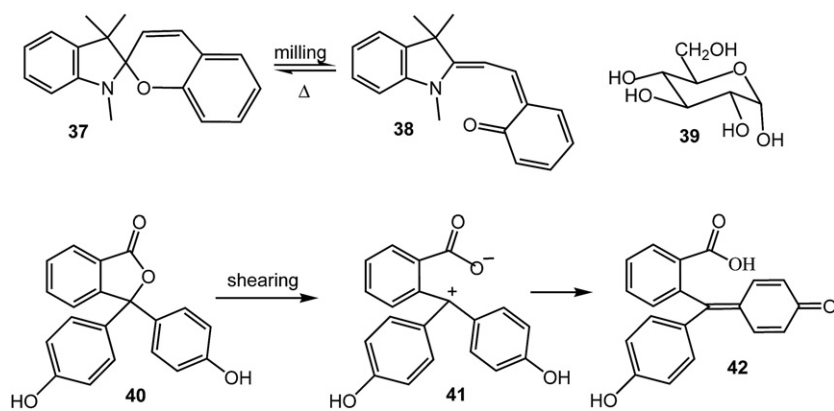
Explosives including liquid ones such as glycerol trinitrate **24** may explode upon mechanical action. Cautious studies of solid samples of the explosive TATB (1,3,5-triamino-2,4,6-trinitrobenzene) **25** were subjected to moderate shock pulses. X-Ray photoelectron investigation indicated that the NO₂ group of TATB was severed from the molecule. This was interpreted as the initiation of shock induced detonation of this material.¹²⁹ Also solid RDX (1,3,5-trinitro-hexahydro-1,3,5-triazine) **26**, TNT (trinitro-

toluene) **27**, and NH₄NO₃ **28** were subjected to shock pulses below the threshold for detonation. The samples were studied by XPS and ESR with respect to breakage or alteration of the internal bonds of these explosives.¹³⁰ The decomposition of RDX **26** by shock waves was also theoretically studied. NO₂ was predicted to be more easily severed than the competing occurrences of [2 + 2]cycloreversion or HONO elimination.^{131,132} Mechanisms for the buildup of explosions in crystals have been summarized.¹⁶

Paraformaldehyde **29** is an atypical solid polymer with weak chain bonds, so that milling degrades the chain very efficiently and completely with mechanochemical formation of the monomer formaldehyde. The degradation of paraformaldehyde **29** is very convenient for the large-scale synthesis of hydroxymethylamines with organic crystalline reagents such as (L)-proline **30**, imidazoles **33**, benzimidazole, *etc.*,⁸ or for the cyclizing methenylation of (L)-cysteine **35**, *etc.* in closed ball mills. The products **31/32**, **34**, and **36** were quantitatively obtained.¹³³ Clearly, these syntheses are genuine examples of stoichiometric organic mechanochemistry, due to the initial mechanical bond breakings of paraformaldehyde. Solid polymer acetaldehyde should behave correspondingly.

Also N/O-acetal bonds as in **37** that are part of a valence isomerization system are weak and can be mechanochemically broken, because the formation of free radicals is avoided (compare the different mechanochemical degradation of cellulose in section 7 and the different situation with **39**). The bond breaking was obtained by grinding the solid spiropyran **37**, which thermally reversible changed its color from bright yellow to intense green by forming **38**.¹³⁴ This valence isomerism at the N/O-acetal carbon is an example of mechanochromism. The weak C–O bond is quite long (1.467 Å; compare 2-*H*-chromene: 1.436 Å) according to easily performed B3LYP/6 31-G* density functional calculations. The variation of the bond strength in such and related systems would allow for the detection of the upper bond weakness limits in milling mechanochemistry of molecular crystals at comparable crystal lattice energies. Completely unrelated are the reasons for not assignable ESR signals from milled α-D-glucose **39** monohydrate and lactose monohydrate at 77 K or room temperature¹³⁵ (milling of iron balls in a glass vessel easily produces surface plasmas!), and the anomerization of glucose **39** by comilling with solid acids¹³⁶ is molecular solid-state chemistry but not “mechanochemistry” as had been claimed by the authors.





rather than a direct mechanical bond breaking. The mechanistic distinction would require preparative-scale verification, or shearing experiments with ESR detection, to exclude mechanisms according to those in section 5. Shearing experiments with weak bond molecules in Bridgman's anvil with ESR characterization and isolation are the methods of choice for unambiguous analyses.

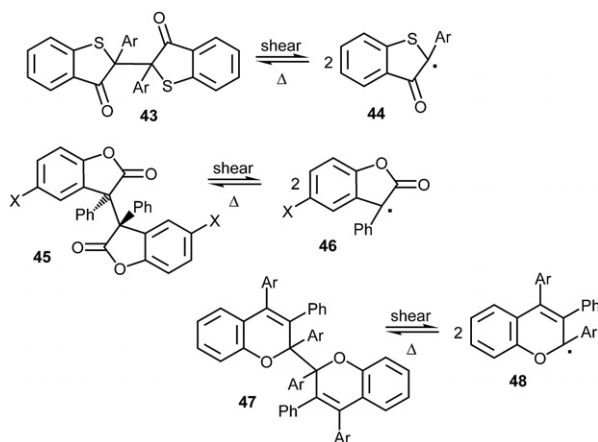
9. Mechanochemistry of strong bonds in small molecules

Non-polymer organic molecules without weak bonds cannot be cleaved by milling, because they escape the mechanical impact by simply being pushed away. If molecular crystals with strong-bond organic molecules are ball-milled, only the weak intermolecular cohesive ligations break while the crystal is cracked. Strong covalent molecular bonds can only undergo mechanochemical breakage by shearing in a Bridgman's anvil at very high pressure, where there is no escape from being pushed away (sonication and shock waving are generally supposed to thermally break strong bonds). The technique with modern equipment is described in ref. 145–147. Mechanochemical reactions of common sized organic molecules at 10 GPa in Bridgman's anvil with shearing rotation have been reported for crystallized benzene, pyridine and derivatives at -70 to -20 °C,^{148,149} or phenanthrene and terphenyls.¹⁵⁰ The molecules cannot escape the shearing under these conditions and the aromatic rings are broken up followed by polymerization of the open-chain species that ensue. Radical intermediates were detected by ESR measurements. Clearly, virtually all organic molecules might be enforced to mechanochemically break bonds under these conditions or even higher pressures that are available. Shearing under high pressure has also succeeded with breaking strong coordination bonds. For example $K_3Fe(CN)_6$ crystals were up to being quantitatively transformed to $K_4Fe(CN)_6$ and unexplored additional products (iron and polycyanogen were suggested) by shearing at pressures of 0.3–5 GPa.¹⁵¹ Overall, six Fe–CN bonds of four potassium hexacyanoferrates(III) were severed to form three potassium hexacyanoferrates(II), leaving one “Fe(0)”

Solid phenolphthalein **40** and several of its substitution products also exhibit a comparatively weak C–O bond that can be mechanochemically broken because of stable triarylmethyl-type cation and carboxylate moiety in the intermediate **41** that stabilizes to **42** by proton shift (**42** is not red in aqueous solution). Such mechanochemical reaction was obtained by plastic deformation in shear at a pressure of 5×10^4 bar.¹³⁷ The red color formed persisted only in the solid state, but not upon dissolution. While the mechanochemical production of triarylmethyl radicals from their (asymmetric) dimers has apparently not yet been reported, various related carbon radicals were mechanochemically produced. The highly hindered dimeric thioindoxyls **43** (Ar = phenyl or substituted phenyl) underwent homolytic cleavage of the central C–C bond upon applying pressure in the solid state to give **44**. The reactivity depended on the substituents on the phenyl ring.¹³⁸ Similarly, the *meso*-bis-(3-phenyl-3*H*-benzofuran-2-one) derivatives **45** (X = H; Cl) exhibited mechano-

chromism by cleavage of the central bond to give **46**.¹³⁹ Related mechanochromism provided the 2,2'-bis(2,3,4-triarylchromenyl) derivatives **47** (Ar = 4-substituted phenyl). They cleaved homolytically the C2–C2' bond when mechanically activated to give green chromenyl radicals **48**.¹⁴⁰ There was also a triphenylimidazolyl dimer that split to the “red dish-purple radical” upon grinding¹⁴¹ and a similar mechanochrome indandione system (**43** with 5-Cl, Ar = *p*-NMe₂C₆H₄, and the “S” exchanged by “C=O”).^{142,143}

Conceptually, also weak coordination bonds in metal complexes might be broken in competition to the comminution of the crystals upon milling. It was concluded that $K_2[PtCl_6]$ lost one of the chlorine atoms upon milling in a glass mill with glass balls to form the Pt(III) complex $K_2[PtCl_5]$ that was detected by ESR spectroscopy.¹⁴⁴ However, the reported loss of chlorine might have occurred by reaction of $K_2[PtCl_6]$ with the surface plasma that is created upon the unavoidable abrasion of glass particles

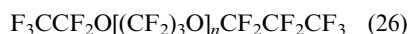
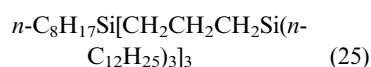
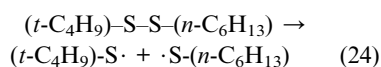


and six “·CN” for additional reactions. These were not thermal reactions due to so-called “very high local temperatures”. It could be shown that tris-(oxalato)-ferrate(III) survived similar shearing at 5 GPa unchanged.¹⁵¹ The temperature rise of the solids was less than 14 K. However, solid-state reductions of hexacyanoferrates(III) by KBr are unrelated and not “mechanochemical”, because no Fe–CN bonds are broken.

The cleavages of covalent bonds by sonochemistry in aqueous solutions are generally considered as thermolysis reactions by cavitation.^{152,153} An example is the 50 kHz sonochemical production of ·CH₃ and ·N(CH₃)CHO radicals from dimethylformamide in water, in addition to the splitting of water, with spin trapping by 3,5-dibromo-4-nitrosobenzenesulfonate.¹⁵⁴ The H· and ·OH radicals formed by the water splitting can initiate a multitude of chemical reactions. However, these are not the subjects of this paper.

Another important way of mechanically breaking strong bonds is efficient friction of molecules between solid surfaces. Automotive brake linings and brake rotors must withstand temperatures up to 800 °C. The linings may consist of composite ceramics, fillers, metals, polymer binders, and slipping agents, but brakes must not be lubricated, except by dry-sliding lubrication using high molecular mass polymers with all effects of continued bond breaking also due to the very high temperatures. Fast running bearings, pistons, saws, drills, *etc.* require lubrication to reduce friction, wear, and metal corrosion. Generally, lubricants consist of mineral oils, or synthetic oils, or natural oils, and additives that adsorb or bind to the moving surfaces. There are both physical and chemical losses of lubricants. The chemical losses subdivide into thermal and mechanochemical destruction, including oxidation. Good lubricants are thermally resistant in their application environment. Mechanical bond breaking of the liquid molecules under friction is a rare event, but it may occasionally occur at asperities of rapidly moving contacting surfaces. Such events are more likely the larger the molecules are, but the lubricant must stay between the surfaces as a thin film and this requires sufficient viscosity. There is, of course, electron emission

from rubbing metals to oil films (mechanoelectricity). Some electrons may be captured by reducible functional groups. However formation of radical anions by triboemitted electrons is not mechanical bond breaking, even though electron transfer can initiate breakage of weak bonds. For example, organic disulfides with efficient load-carrying anti-scuffing properties can be used as highly effective oil additives. They would easily dissociate after capture of an electron to give RS[·] and RS⁻. However, weak disulfide bonds of molecules are also mechanochemically broken under the given conditions to yield two thiyl radicals (24) that react with many metal surfaces to generate closed monolayers. The anti-wear activity of nonsymmetrical alkyl disulfides was found better than that of linear ones,¹⁵⁵ because the nonsymmetrical additive did not readily arrange in a solid-like structure of a few confined molecular layers.



The base oils have to be chosen according to the required heat stability. Stable bonds are present in the depicted silahydrocarbon 6-88-134 (25) with unique anti-wear properties, high viscosity, very low volatility and ability to solubilize conventional additives,¹⁵⁶ or in the perfluoroalkylethers (PFPAEs) (26), where Demnum S 20 ($n = 20$) is a high speed civil transport hydraulic fluid,¹⁵⁷ or in mineral oils and natural oils (triglycerides). They will hardly be broken in lubrication environments unless micro-particles of ceramics or metals are abraded and cracked. The particles' surface plasma or their coordinately unsaturated surface will be eagerly saturated by abstraction of H or F atoms from the lubricant. The organic radicals thus formed will undergo their stabilization reactions. This could, of course, be studied by destructive milling with cracked ceramics or metals in the early stages. As a consequence, the addition of anticorrosive agents for eliminating the risk of metal oxide formation by corrosion is required, to fight the detrimental

effect of wear. Common corrosion inhibitors are zinc dialkyl or zinc diaryl dithiophosphates (RO)₂P(S)S₂ZnS(S)-P(OR)₂ that may cleave one of the S–Zn bonds and form protective lamellar aggregates and sulfide tribofilms.¹⁵⁸ Tribofilms are also formed by diphenyl phosphate.¹⁵⁹ A different concept used the addition of 13,14-dihydroxydocosanoic acid CH₃(CH₂)₇CH(OH)-CH(OH)(CH₂)₁₁CO₂H, DHDA that forms a monomolecular tribofilm on the frictional surface of the hydroxide surface layers of metals in air by esterification.¹⁶⁰ The formulation of additives in lubricants for diverse applications is an actively studied complex field of tribology and well-understood mechanochemical principles shall be highly supporting.

10. Single bond breaking and nano-dissection

This section deals with mechanochemistry at the single molecule level with dynamic force AFM and mechanical nanodissection with AFM. The pull-off technique (single-molecule force) has been outlined.¹⁶¹ An AFM tip is covered with gold and bound to molecules of interest *via* a tether with thiol end group to form a unimolecular layer. The other ends of the tip molecules or different molecules are similarly bound to a gold surface. These form bridges or they are contacted to form a few bonds between the sharp tip molecules and the surface molecules. Bond forces can be obtained from the measurement of dynamic force curves that exhibit steps as multiples of the smallest one-bond rupture force. These techniques work for weak and intermolecular bonds. The breaking forces of intermolecular bonds are cited here with some examples to demonstrate the very high sensitivity down to a few pN forces, how the technique can be used for the breaking mechanism of weak covalent bonds, and how weak and strong bonds compare. For example, the coordinate binding forces of tethered histidine (of a 6 units peptide) and nitrilo triacetic acid complexes of Ni²⁺, Co²⁺, Cu²⁺, Zn²⁺ varied from 22 ± 4 pN (Co) to 58 ± 5 pN (Cu) at a loading rate of 0.5 μm s⁻¹,¹⁶² or the binding force in tethered ferrocene/β-cyclodextrine host–guest complex was 56 ± 10 pN.¹⁶³ The rupture of the charge transfer complex between

tethered *N,N,N',N'*-tetramethyl-*p*-phenylenediamine and 7,7,8,8-tetracyanoquinodimethane required 70 ± 15 pN force.¹⁶⁴ Immobilized immunoglobulin G and surface protein adhesion on living *Staphylococcus aureus* (trapped in a filter pore) exhibited a binding force of 64 pN.¹⁶⁵ The binding force for integrin and fibronectin increased from 34 to 39 pN after histamine treatment.¹⁶⁶ The long known biotin with avidin or streptavidin interaction was revisited at changed immobilization (silanation and glutaraldehyde bonding) at various force loading rates.¹⁶⁷ As expected (but contrary to earlier reports), the binding force with avidine was found stronger (by about 20 pN) than the one of streptavidin (200 pN at a rate of 1267 pN s⁻¹). Interestingly, also the differentiation of enantiomers with a chiral tip-molecule was possible. Force ratios of 1 : 2 and 1 : 3 for the two enantiomers by measurements in ethanol allowed chiral recognition.^{161,168}

Covalent weak disulfide bonds of an octameric protein with 8 disulfide bonds were immobilized between a surface and an AFM tip and stretched with various forces below the breaking level to obtain rate constants for thiol-initiated and phosphine-initiated reduction into thiols. Such reduction depended exponentially on the constant force settings. Arrhenius type treatment revealed $F\Delta x/kT$ exponents. The found Δx values of 0.31 and 0.44 Å for thiol and phosphine reductants, respectively, were interpreted as bond elongations at the transition states of these disulfide reductions.¹⁶⁹ A solvent effect on Δx was also reported. The single molecule method is a promising start for gaining molecular level understanding of chemical reactivity at the sub-Å level. It is however a mechanophysical technique as long as mechanical bond breaking has not occurred.

Strong single covalent bonds in molecular bridges between tip and surface can not be mechanically studied with the thiol to gold immobilization technique, because the Au–S or Au–Au bonds break already at forces of 1.5 nN.¹⁷⁰ A reported Au–S value of 2.2 nN for an Au-S-terminated polymethacrylic acid single polymer chain is probably too large.¹⁷¹ Si–O anchored polydimethylsiloxane bridges (average length: 360 nm) revealed binding forces probably for the Si–O bond of the siloxane of 1.34 nN.¹⁷² A binding force of 2.0 ± 0.3 nN was found for a C–Si bond¹⁷³

and 2.1 ± 0.3 nN for a Si–Si bond between surface and AFM tip.¹⁷⁴ A detailed description of the proper extraction of the bond parameters has appeared.¹⁷⁵ A description of the additional informations that are gained below bond breaking (elasticity, conformation, *etc.*) is also available.¹⁷⁶

Unlike mechanical microdissection¹⁷⁷ the nanodissection with an AFM tip allows for space specific separation and nanoshuffling of molecular fragments for separate investigation.¹⁷⁸ This includes the nanodissection of protein complexes from membranes^{179,180} and the extraction of chromosomal DNA for gene analysis.¹⁸¹ Single- and double-stranded DNA was repeatedly dissected with an AFM tip and imaged.¹⁸² Nanodissection and picking up of stretched DNA strands on a properly coated mica surface was realized at the desired position by fine tuning of the force between the AFM tip and the DNA sample. The fragments could be picked up and amplified. These mechanochemical techniques have potential in clinic diagnosis or positional cloning of genes and they offer viable strategies for ordered DNA sequencing.¹⁸³

11. Conclusions

A strict and clear-cut systematics of mechanochemistry that separates out mechanophysical events and clearly distinguishes mechanochemistry from molecular solid-state chemistry removes widespread confusion by undue claims in the literature, and it is required for a stringent description of the important field in various sections. Such endeavor achieves the due order in a very diverse field. Mechanochemistry covers bond breaking by mechanical activation of infinite covalent crystals, metals, polymers, weak-bond molecules, and strong-bond molecules at the extreme confinement of Bridgman's anvil. Common strong-bond solid-state molecular chemistry is not "mechanically activated" but chemically driven, despite numerous undue literature claims. The systematic differentiation opens new horizons for the diverse branches of mechanical action to reactive solids in an easily comprehensible way. Ball mills and the other mechanical devices are multi-purpose tools, but this favorable situation cannot dispense with the mechanistic distinction of the very

different applications. Only the mechanochemical milling produces sparkling plasmas and radicals by covalent bond breaking, and there are also instances of mechanochemical bond breaking without radical or zwitterion formation to give energetic products for waste-free organic syntheses. The self-evident differentiation has important practical consequences for the optimization of the mechanical impact that must be high enough for mechanochemistry, which must mechanically break intramolecular bonds. However clotting at too high impact or temperature must be avoided, because kneading instead of milling would follow. The preparative and technical applications of mechanochemistry in its well-defined form are highly varied. The easily generated surface plasmas are used for low temperature production of ceramics and nanotubes, scratch-less polishing, leaching, grafting of nanoparticles, wastes remediation, *etc.* The radical formations by bond breaking are used in polymer technology or in weak- and strong-bond chemistry including explosives, radical chain initiation, lubricants, and wear protection. Also pulling single bond breaking and cutting nano-dissection for gene technology are of high importance. The sound mechanistic awareness recognizes the fantastic possibilities of well-defined mechanochemistry that will continue to mature and flourish.

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