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On the applicability of solventless and solid-state reactions to the meteoritic chemistry

Vera M. Kolb

Department of Chemistry, University of Wisconsin-Parkside, Kenosha, WI 5314, USA
e-mail: kolb@uwp.edu

Abstract: Most chemical reactions on asteroids, from which meteors and meteorites originate, are hypothesized to occur primarily in the solid mixtures. Some secondary chemical reactions may have occurred during the periods of the aqueous alteration of the asteroids. A myriad of organic compounds have been isolated from the meteorites, but the chemical conditions during which they were formed are only partially elucidated. In this paper, we propose that numerous meteoritic organic compounds were formed by the solventless and solid-state reactions that were only recently explored in conjunction with the green chemistry. A typical solventless approach exploits the phenomenon of the mixed melting points. As the solid materials are mixed together, the melting point of the mixture becomes lower than the melting points of its individual components. In some cases, the entire mixture may melt upon mixing. These reactions could then occur in a melted state. In the traditional solid-state reactions, the solids are mixed together, which allows for the intimate contact of the reactants, but the reaction occurs without melting. We have shown various examples of the known solventless and solid-state reactions that are particularly relevant to the meteoritic chemistry. We have also placed them in a prebiotic context and evaluated them for their astrobiological significance.

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Introduction and background

One of the important goals of astrobiology, as outlined in the NASA's Astrobiology Roadmap, is to determine the history of the prebiotic chemical ingredients that are important for habitable environments and which could sustain living systems (Des Marias *et al.* 2008). Myriads of organic compounds have been found on the carbonaceous chondrites meteorites, such as Murchison (Cronin & Chang 1993; Cronin 1998; Cronin *et al.* 1995; Kerridge 1999; Sephton & Gilmour 2000; Cooper *et al.* 2001; Sephton 2002; Shaw 2006; Schmitt-Kopplin *et al.* 2010). Tens of thousands of different molecular compositions have been revealed on Murchison by the application of ultra-high resolution analytical methods that combine state-of-the-art mass spectrometry, liquid chromatography and nuclear magnetic resonance (Schmitt-Kopplin *et al.* 2010). Meteorites are obtained from meteoroids, and the latter from asteroids (Kerridge 1999; Shaw 2006). Meteorite is a solid body of extraterrestrial material that survives passage through the Earth's atmosphere and reaches the ground. This definition can be expanded to include Martian and Lunar meteorites (Rubin & Grossman 2010). Meteors are objects entering the Earth's atmosphere that burn up completely during the passage through the upper atmosphere. They are also known as 'shooting stars' (Shaw 2006). Meteoroids are natural solid objects (typically <10 m across), which are moving in the interplanetary space, before they enter the Earth's (or other planetary) atmosphere (Shaw 2006; Rubin & Grossman 2010). Thus, meteors and meteorites are derived from meteoroids. Asteroids, also known as 'minor planets', are small solar-system bodies (typically tens of metres to almost 1000 km across) that orbit around the Sun, mainly between the orbits of Mars and Jupiter. They are classified by their characteristic composition/spectra to carbon-rich (C-type), stony (S-type) and metallic (M-type) (Chapman 1999; Seeds 1994; Asteroid 2011).

Chemistry on asteroids is considered important for the early chemical evolution (Lurquin 2003; Glavin *et al.* 2010; Abramov & Mojzsis 2011). Water on asteroids was available only during the periods of aqueous alteration (Kerridge 1999; Bland *et al.* 2009). However, most organic materials are not water soluble. Thus, even though water became periodically available, it is not clear how this would help the water-insoluble materials to react. Some of the problems of the organic synthesis on asteroids or meteoroids can be solved by borrowing the knowledge from a new and emerging field of green chemistry (Anastas & Warner 2000; Lancaster 2002; Lankey & Anastas 2002; Doxsee & Hutchinson 2004), which is environmentally friendly. Since most organic reactions require an organic solvent, which may be toxic, running the reactions without solvents is considered beneficial to the environment. Various chemical procedures that do not utilize organic solvents have been developed by the green chemists. In this paper, we propose that many reactions on meteorites could occur as solventless (Tanaka & Toda 2000; Cave *et al.* 2001; Raston 2004; Tanaka 2009) or solid-state reactions (Thomas 1979; Toda *et al.* 1990; Toda 1995; Rothenberg *et al.* 2001; Kaupp 2005). We have previously explored some of these reactions in the astrobiological context (Kolb 2010a, b). This paper is an expanded and revised version of a preliminary paper that was published in a conference proceeding (Kolb 2010b).

Solventless and solid-state reactions

Chemists have recently explored the so-called solventless reactions (Tanaka & Toda 2000; Cave *et al.* 2001; Raston 2004; Tanaka 2009), which are green by virtue of not needing any solvents at all. For example, as the solid reaction components are mixed together, the melting point of the mixture becomes lower than the melting points of its individual components. In some cases, the entire mixture may melt upon mixing. The reactions could then occur in a viscous liquid state.

The principle is that of the 'mixed melting point', which is the lowering of the melting point of a pure component, when another component is added to it (Cave *et al.* 2001; Raston 2004). This is due to the incorporation of the impurities into the crystalline lattice of the compound, which breaks up the regular crystalline pattern. When more impurities are present, the melting point becomes even lower. Yet another scenario is to grind together the solid reactants, without melting them (Thomas 1979; Toda *et al.* 1990; Toda 1995; Rothenberg *et al.* 2001; Kaupp 2005). Such a ground mixture may become reactive. Sometimes mild heating can be employed to speed up the reactions. These are solid–solid reactions. Another way is to use a liquid and a solid component, and grind them together. The suspension may then become reactive. Sometimes a gas–solid reaction is successful. All these scenarios could be fruitful on asteroids. Our main focus is on the solventless and the solid–solid reactions. Some asteroids, such as the C-type (Chapman 1999; Seeds 1994; Asteroid 2011) are rich in the organic compounds, judging also by the analysis of Murchison and similar carbonaceous chondrites (Cronin & Chang 1993; Cronin 1998; Cronin *et al.* 1995; Kerridge 1999; Sephton & Gilmour 2000; Cooper *et al.* 2001; Sephton 2002; Sephton *et al.* 2002; Shaw 2006; Schmitt-Kopplin *et al.* 2010). Some of these compounds may be reactive towards each other, but some others may not be. However, the unreactive compounds could lower the melting points of the reactive ones, enabling the reactions to occur in the melted state. We have shown this in the example of the solid-state Diels–Alder reaction between anthracene-9-methanol and N-methylmaleimide to which we have added an unreactive third component, naphthalene (Fuller & Kolb 2011). The temperature estimates on the asteroids include a range from 25 to 100 °C, which is consistent with aqueous alterations (Kerridge 1999) and is friendly to preservation of the organic compounds. The heat is provided by the radioactive processes or impacts (Kerridge 1999). This temperature range is fortuitously also a typical range for many standard organic reactions that are performed in the laboratory.

Representative examples of astrobiologically relevant solventless and solid-state reactions

A substantial body of the literature illustrates that many organic reactions occur as solventless (Tanaka & Toda 2000; Cave *et al.* 2001; Raston 2004; Tanaka 2009) or in the solid state (Thomas 1979; Toda *et al.* 1990; Toda 1995; Rothenberg *et al.* 2001; Kaupp 2005). They often occur rapidly and with remarkable efficiency (Toda 1995; Kaupp 2005). Examples include all major types of organic reactions, such as oxidations, reductions, eliminations, substitutions, condensations, cyclizations, rearrangements, formation of carbon–carbon, carbon–oxygen and carbon–nitrogen bonds, among many others. Detailed experimental procedures for solvent-free reactions are compiled in a recent book (Tanaka 2009). Many such procedures are either completely prebiotic, or could be made prebiotic rather easily. However, the real velocity of the reactions should be tested in planetary chambers under interplanetary conditions. This fortunate fact was not addressed in the book, which emphasis is a general organic synthesis. Especially interesting is the formation of ethers in the solid state, from the solid mixture of the alcohols and acid catalysts (Toda *et al.* 1990). Such a synthesis could be a prebiotically feasible way to produce various ethers. Such ethers could be used as membranes for the primitive organisms. While most contemporary organisms use lipids that are esters (Voet *et al.* 2006), some archaea's membranes are ethers (De Rosa *et al.* 1986; Kates 1993). Other interesting examples include syntheses of large molecules that are related to porphyrins. These and other examples are presented below, with the chemical equations and essential conditions. They illustrate a great potential for prebiotic chemistry and should be investigated further in this context. All the examples come from Tanaka (Tanaka 2009), who cites all the primary references. Additional references are cited if they provide more details about the procedures and to show the prebiotic significance that was not addressed by Tanaka.

Oxidation of alcohols to aldehydes

We show an example of oxidation reaction in which alcohols are oxidized to aldehydes in a liquid/gas or a solid/gas reaction. We are not arguing here for the prebiotic role of the NO_2 gas (Fig. 1). Instead, the prebiotic significance of this reaction is that the available equivalent prebiotic gaseous oxidizing agents could have worked in an analogous way. Aldehydes are an important group of reactive molecules which can lead to various complex prebiotic molecules. For example, the Maillard reaction, which occurs between the sugar aldehydes and the amino acids, results in a myriad of complex molecules (Kolb *et al.* 2005, 2006; Kolb & Bajagic 2006a, b). The astrobiological importance of the Maillard reaction is very high since the starting materials are definitively prebiotic. Sugars can be formed by prebiotic means (Kim *et al.* 2011; Ricardo *et al.* 2004; Lambert *et al.* 2004, 2010). The sugar-related molecules have been found on meteorites (Cooper *et al.* 2001). The amino acids are the ubiquitous

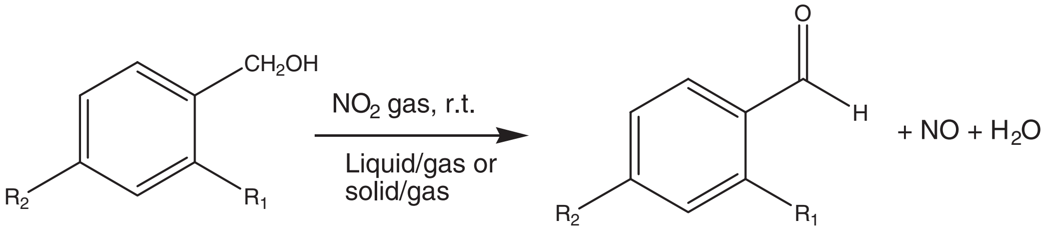

Fig. 1. Oxidation with NO_2 gas (Tanaka 2009, p. 31).

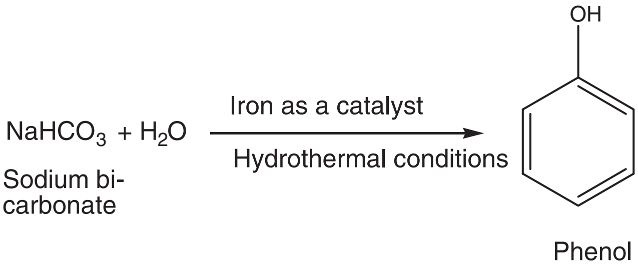

Fig. 2. Prebiotic synthesis of phenol (Tian 2007).

prebiotic molecules (Miller 1953, 1955; Fitz *et al.* 2007), which are abundant on the meteorites (e.g. Cronin *et al.* 1995; Sephton 2002).

Carbon–carbon bond formation by the oxidative coupling of phenols

Prebiotic and thus astrobiological significance of phenols was established (Hayatsu *et al.* 1980; Tian *et al.* 2007; Kolb & Liesch 2008). A synthesis of phenol by treatment of sodium bicarbonate with water and iron as a catalyst under hydrothermal conditions was reported (Tian *et al.* 2007) and is shown in Fig. 2.

This synthesis has placed phenol on the map of the compounds that were feasible on the prebiotic Earth, or other planets in which hydrothermal conditions exist or have existed.

An example of the oxidative coupling of phenols, which results in the formation of a carbon–carbon bond, is shown in Fig. 3. It can occur as a solid-state reaction. The molecule obtained, so-called 'binol' ([1,1′-binaphthalene]-2,2′-diol), is not planar due to the steric hindrance. Instead, it is twisted and thus asymmetric, which makes it chiral (Carey & Sundberg 2007). This molecule is obtained in the laboratory as a racemic mixture of two enantiomers, which can be separated, for example by the chromatography with a chiral stationary phase. We have checked the procedure for the formation of binol in our laboratory. It works really well, as described. Under the prebiotic conditions enantiomeric enrichment can be achieved perhaps under the influence of the available chiral molecules or minerals. Thus, the prebiotic synthesis of binol is important since it has a good potential for the development of enantiomeric selectivity on the prebiotic Earth (Fig. 3).

Formation of ethers under the solid-state conditions

Formation of ethers by condensation of alcohols is not favourable in the aqueous solution. However, this reaction works well in the solid state with the solid p-toluene sulfonic acid (TsOH) as a catalyst (Toda *et al.* 1990). One such example is shown in Fig. 4. We have reproduced this experiment in our laboratory. It works really well, especially if anhydrous TsOH is used or is created *in situ* by a mild heating of the commonly available TsOH hydrate in the reaction mixture.

Such solid-state synthesis could be prebiotically feasible. The use of TsOH as a catalyst can probably be substituted by various acidic clays (Fig. 4).

Ethers may have been used as primitive membranes in the original organisms. Even today some archaea use ethers as membranes (De Rosa *et al.* 1986; Kates 1993). However, most contemporary organisms use lipids, which are esters, as their membranes (Voet *et al.* 2006).

Formation of esters in the solid state

Esterification reaction between alcohols and carboxylic acids is reversible. It produces the desired ester and water. The equilibrium of the reaction needs to be shifted towards the ester product. Thus water should be removed. In the organic laboratory, water can be removed by using concentrated H_2SO_4 as a catalyst and a dehydrating agent, or by use of the contraptions such as Dean–Stark trap, which remove water (e.g. Harwood *et al.* 1999). Neither procedure is prebiotic, since it involves intervention. However, the solvent-free esterification is shown in Fig. 5 appears prebiotically feasible. Perchlorates, which catalyse this reaction, are found on Earth, especially under arid conditions (Duncan *et al.* 2005; Navarro-Gonzáles *et al.* 2003), and also on Mars (Hecht *et al.* 2009).

Another prebiotically feasible solid-state esterification is that of cholesterol. The ester thus obtained, shown below, could perhaps have served as a primitive lipid membrane (Fig. 6).

Aldol condensations

Aldol-type condensation reactions, which form carbon–carbon bonds, play an important role in chemistry (e.g. Laue & Plagens 2005) and biology, e.g. in the citric-acid cycle (e.g. Bettelheim *et al.* 2004). Aldol reactions under solventless, solid–solid and solid–liquid conditions, with various catalysts, have been reviewed by Tanaka (2009). An example in which basic alumina is used as a catalyst, under solvent-free conditions, follows (Fig. 7).

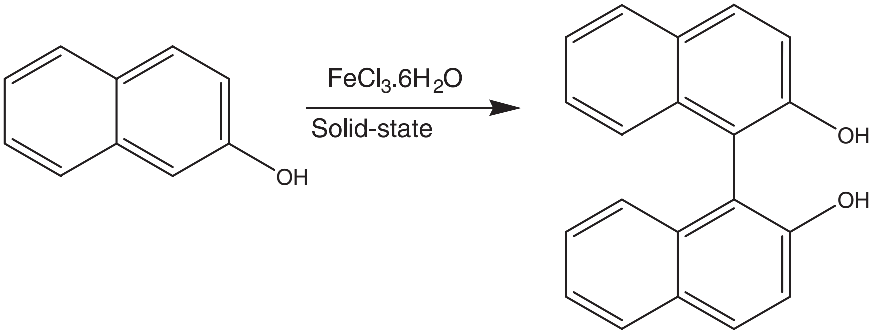

Fig. 3. Oxidative coupling of a phenol (a naphthol) to a binol (Tanaka 2009, p. 33).

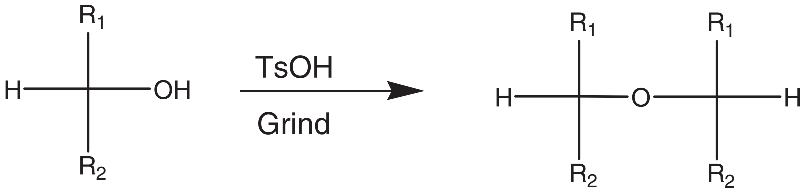

Fig. 4. Solvent-free etherification reaction (Tanaka 2009, p. 276).

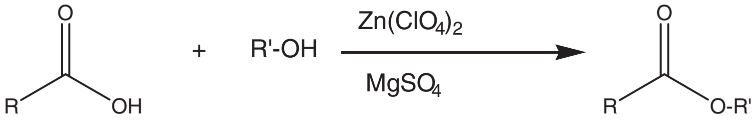

Fig. 5. Solvent-free esterification (Tanaka 2009, p. 288).

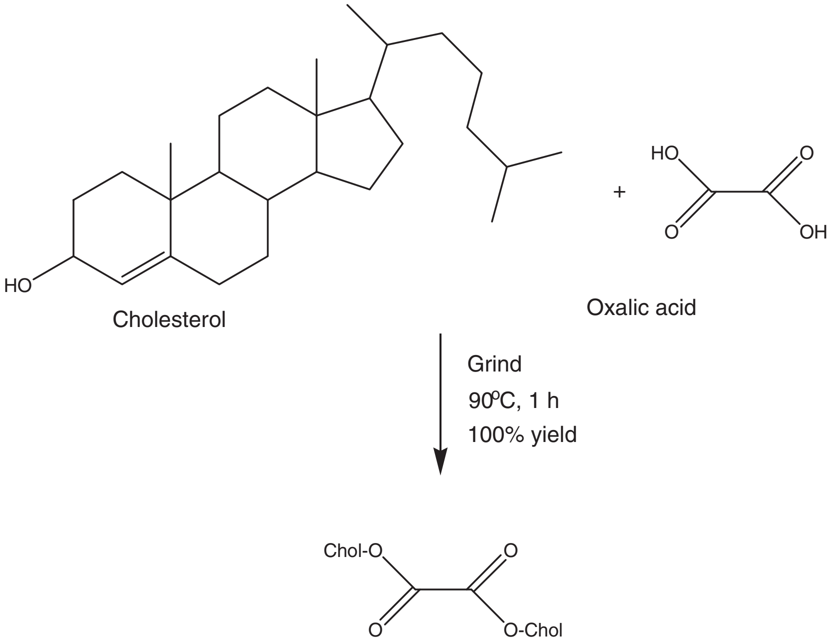

Fig. 6. Cholesterol solid–solid esterification (Tanaka 2009, p. 431).

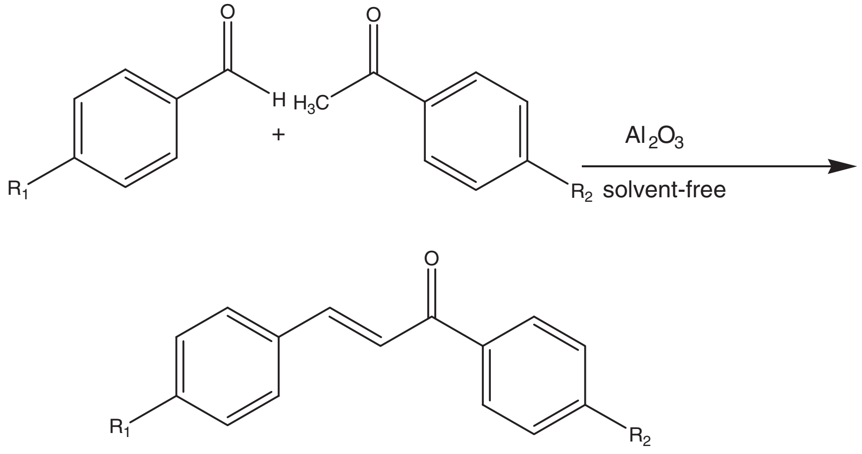

Fig. 7. Aldol condensation with basic alumina (Tanaka 2009, p. 39).

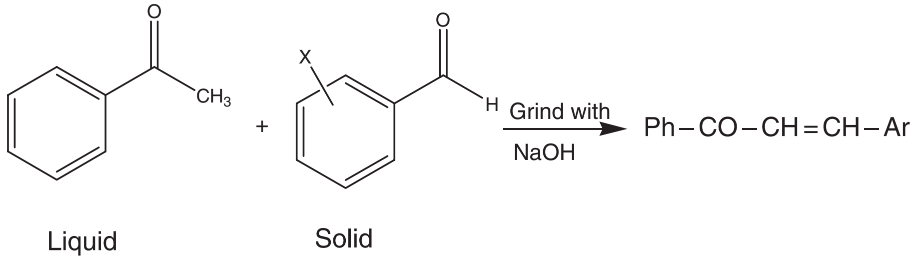

Fig. 8. Liquid–solid aldol reaction (Tanaka 2009, p. 40).

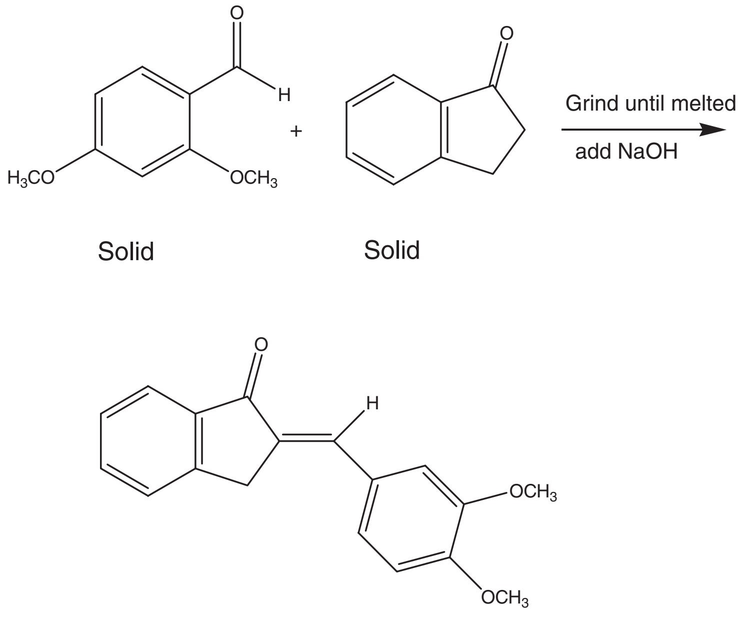

Fig. 9. Aldol reaction in a melted state (Tanaka 2009, p. 45).

Another example of aldol reaction, this time with NaOH, is performed under solventless conditions. One component is a liquid and the other is a solid. They are made reactive by grinding (Fig. 8).

The solventless aldol reaction in which two solids melt upon grinding is shown in Fig. 9.

Solventless synthesis of corrole

A rather spectacular synthesis follows, in which a corrole, a porphyrin analogue, is formed. The reaction occurs under solventless conditions. Corrole could serve as a primitive enzyme, since it has a metal complexing site in the centre of the molecule (Fig. 10).

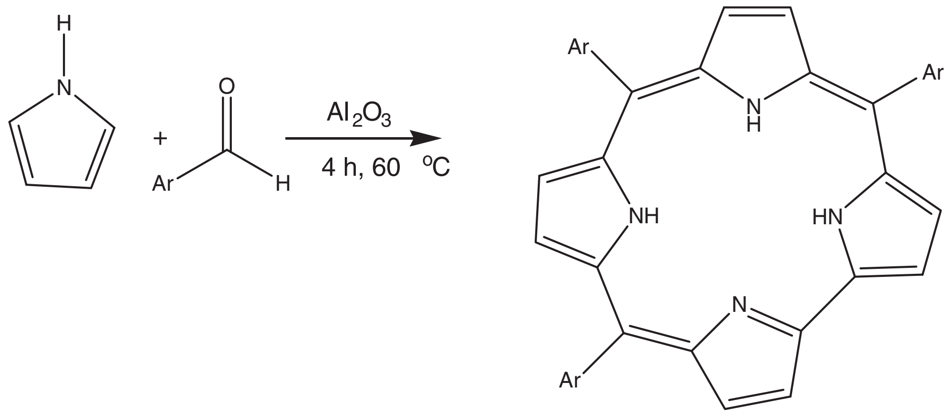

Fig. 10. Solventless condensation of pyrrole and aldehyde to a corrole (Tanaka 2009, p. 43).

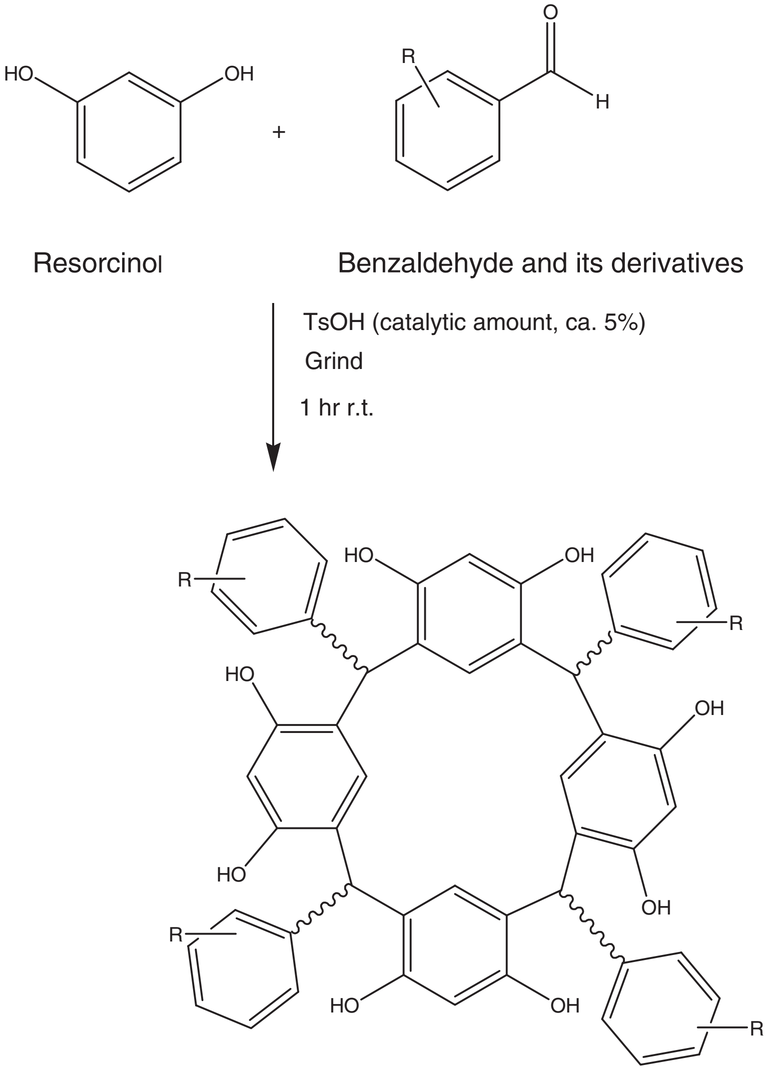

Fig. 11. Resorcinol/aldehyde solvent-free cyclocondensation to a macromolecule with a cavity (Tanaka 2009, pp. 50–51).

Synthesis of a macromolecule with a cavity

It is often difficult to get a high yield of well-defined macromolecular materials in the aqueous solution. The example below illustrates success of the solid-state chemistry. The large cyclic molecule that is formed could perhaps serve as a primitive enzyme on the account of its cavity. The TsOH could perhaps be substituted with some acidic clay (Fig. 11).

Conclusions

In this paper, we show how the recent advances in the solventless and solid–solid reactions, which have been made mostly for the green chemistry applications, can be successfully applied to the chemistry on asteroids and meteors. We have shown selected examples of the key organic reactions that occur with ease in the solventless and solid-state media, and have placed them in a prebiotic context and evaluated them for their astrobiological significance. Especially important are esterifications and etherifications, since they are relevant to the production of the prebiotic lipid membranes, and the aldol-type condensations that are relevant to the carbon–carbon bond formation and the citric-acid cycle. Preparations of the large cyclic molecules that could serve as primitive enzymes have also been achieved. Some of the reactions provide chiral molecules, such as binols, which could eventually be enantiomerically enriched by the clays or some other means. The reactions that we have shown are generally not amenable to the aqueous prebiotic pathways. However, they are uniquely well suited for the solid state or solventless chemistry that could occur on the asteroids and meteoroids.

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