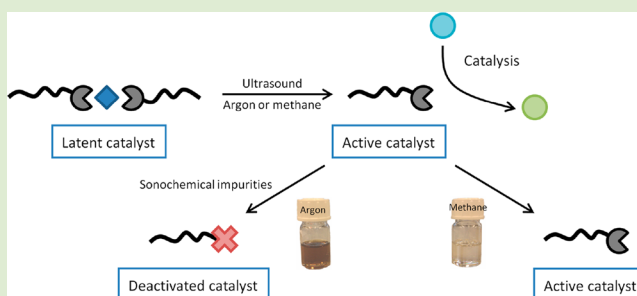# Performance of Mechanochemically Activated Catalysts Is Enhanced by Suppression of the Thermal Effects of Ultrasound

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S Supporting Information

ABSTRACT: In this work, we demonstrate that the performance of mechanochemically activated transesterification and alkene metathesis catalysts is significantly enhanced when the thermal effects of ultrasound are suppressed. Suppression of these effects is realized by performing the reaction under methane instead of argon. Not only do these results provide further confirmation of the true mechanochemical nature of the ultrasonic activation of the catalysts, but it also strongly recommends the use of methane as standard saturation gas when studying the mechanochemical effects of ultrasound.

The use of mechanical forces to activate chemical bonds ("mechanochemistry") and to perform chemical transformations is receiving increasing attention.[1−4] Mechanically activated reactions are of interest because they may display reaction pathways and product distributions that are completely different from the corresponding thermally or photochemically activated reactions.[5] Furthermore, mechanochemistry opens numerous new possibilities, such as mechanical signal transduction and autonomous self-healing materials.[6] To transfer sufficient force onto the reactive bond, the reactive unit (mechanophore) should be placed within a polymer chain.[7,8]

Ultrasound is the most commonly used technique to apply mechanical forces on polymer chains in solution. The rapid collapse of cavitation bubbles in solution, generated by the acoustic pressure wave, creates local regions of high fluid strain that cause polymer chains to unfold and eventually break.[9,10] In addition to mechanical effects caused by the large elongational forces, other sonochemical effects are known to occur. Thermal effects, comprised of radical formation due to pyrolysis of volatile (solvent) molecules and their subsequent reactions, occur within the hot-spot.[11] Previously, we, and others, have shown that thermal effects can be suppressed by choosing saturation gases with a relatively high heat capacity, such as methane.[11−13] A high heat capacity results in lower hot-spot temperatures and, hence, lower radical production, whereas the mechanical effects are not significantly affected.

Mechanical forces induced by ultrasound have been used to activate latent catalyst complexes. We have reported on the use of organometallic complexes of silver(I) and ruthenium(II) coordinated by two N-heterocyclic carbene (NHC) ligands, which are functionalized with a poly(tetrahydrofuran) (PTHF) chain (Scheme 1).[3,14] These polymer complexes are inactive, but after mechanically induced dissociation of one of the NHC ligands, they become active catalysts for, for example, transesterification reactions,[16] ring-opening polymerizations of

lactides,[15] or alkene metathesis reactions.[17] More recently, Bielawski and co-workers reported on mechanocatalysis with polymer palladium(II)−pyridine complexes[18] and metal-free polymer pyridine−boronium complexes as latent catalysts.[19]

In this work, we show that the use of a saturation gas with a high heat capacity in ultrasonically activated mechanocatalysis enhances the catalytic performance by suppression of thermal side reactions. At the same time, the results provide further confirmation of the true mechanochemical nature of the activation process, because a lower performance would be expected if thermal effects were responsible for catalyst activation.

We recently reported about mechanochemically activated catalysis of transesterification.[3] The transesterification of vinyl acetate (VAc) with benzyl alcohol (BnOH) is used as a benchmark reaction for studying the mechanocatalyst activity (Scheme 1).[16] The products of this transesterification reaction are benzyl acetate (BnAc) and vinyl alcohol. Rapid tautomerization of vinyl alcohol to acetaldehyde prevents the reverse reaction and shifts the equilibrium toward product formation. Recently, we observed a strong concentration-dependence of the catalytic activity of catalyst **1**, which was ascribed to the consumption of activated carbene species by low concentrations of sonochemically produced impurities.[20] It is well-known that the sonication of solutions leads to the formation of reactive species, such as radicals.[11] In earlier work,[12] we have demonstrated the purely mechanochemical nature of catalyst activation. However, it is plausible that radicals produced by sonication, or the secondary products of these radicals (here referred to as thermal impurities), deactivate the highly reactive

Scheme 1. Overview of Latent Mechanocatalyst Complexes and Catalytic Reactions Studied in this Work[a]
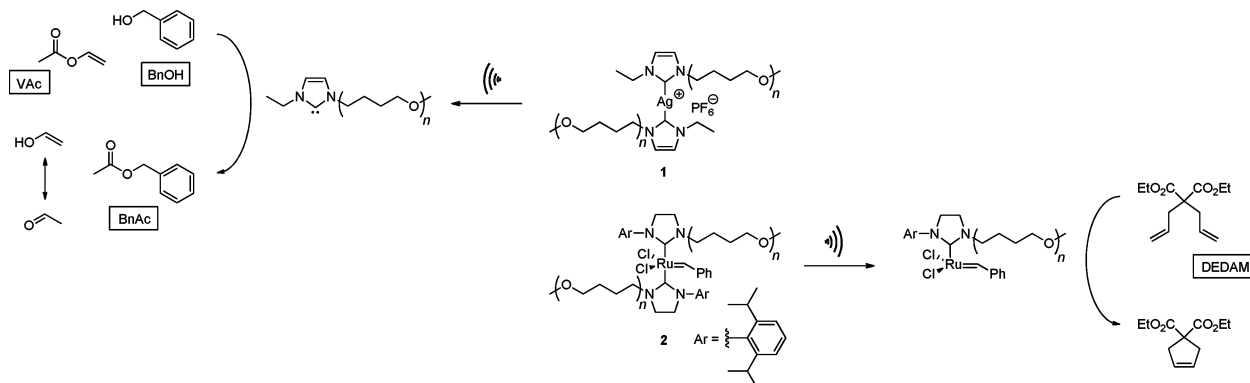
[a]Left: transesterification of vinyl acetate (VAc) with benzyl alcohol (BnOH) using the silver(I) catalyst complex **1**. Right: ring-closing metathesis (RCM) of diethyl diallyl malonate (DEDAM) using polymeric alkene metathesis catalyst **2**.

NHCs. In this respect, mechanocatalytic experiments under radical-suppressing conditions were a logical method to test this hypothesis. We have shown that the use of methane as the saturation gas in place of argon results in a significant decrease in radical production while the scission rate of the polymer catalyst complex remains the same.[12] Therefore, we performed mechanocatalytic experiments under argon and methane as saturation gases. Solutions of **1** in a mixture of toluene, BnOH, and VAc (in a volumetric ratio of 5:2:3, see also Supporting Information) made up to different concentrations were sonicated for 1 h using either argon or methane as the saturation gas.[21] By comparing the data summarized in Table 1,

Table 1. TON of the Transesterification Reaction for Different Concentrations of Catalyst Complex 1 under Argon and Methane

	TON after 30 min sonication	
concentration **1** (mM)	argon	methane
0.25	10	20
0.50	20	380
0.75	60	480
1.0	130	not determined

it is evident that suppressing thermal effects in sonochemistry leads to strongly increased turnover numbers in mechanocatalytic transesterification reactions. A significant increase in catalyst activity is observed already at a catalyst concentration of about 0.25 mM. At higher catalyst concentrations (ca. 0.50 and 0.75 mM), a dramatic increase of the TON from about 20 and 60 to approximately 400 and higher was observed when changing from argon to methane as the saturation gas.

Under methane, catalyst complex **1** was significantly more active, even at lower concentrations where hardly any catalytic activity was observed under argon. The increase in catalyst activity reflects the enhanced survival probability of the free NHCs when suppressing secondary sonochemical processes, which in turn results in higher steady state concentration of the active species.

To investigate the general applicability of this approach for increasing the efficiency of sonochemically activated catalysis,

we also compared the ring-closing metathesis (RCM) reaction of diethyl diallyl malonate (DEDAM) using alkene metathesis catalyst **2** (see Scheme 1) under argon and methane. Under argon, a scission rate (k_{sc}) of 8.3×10^{-3} min^{-1} was observed and a DEDAM conversion of 34% (TON = 340) after 75 min (Figure 1), which is in line with earlier reports.[14] Under
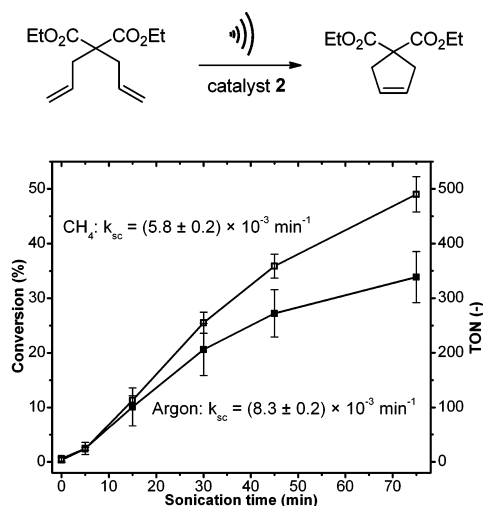

Figure 1. Time−conversion plot for the ring-closing metathesis of DEDAM using polymeric alkene metathesis catalyst **2** sonicated under argon (closed symbols) and methane (open symbols). The concentration of **2** was 0.20 mM and 1000 equiv of DEDAM with respect to the catalyst were used.

methane, and with an identical energy input, a 30% lower scission rate was observed ($k_{sc} = 5.8 \times 10^{-3}$ min^{-1}). This can be ascribed to the slightly higher solubility of methane compared to argon in toluene. The greater solubility helps to cushion the collapsing cavitation bubbles resulting in slower polymer scission.[12,13] In view of the lower catalyst activation, it was striking to observe a significantly higher conversion (49%, TON = 490) with methane as saturation gas.

To further investigate the nature of the impurities responsible for the observed effect, both the transesterification and the metathesis reaction mixtures were first sonicated without catalyst under argon and under methane for 20 or 75 min. The appropriate catalyst complex (**1** or **3**) was then added to the presonicated solutions and subsequently heated in order

to thermally activate the catalyst. Model catalyst complex **3** (see inset of Figure 3 for structure) was used since it was shown in previous work[14] to have similar thermal catalytic activity compared with polymer catalyst complex **2**. In both cases, the solutions sonicated under argon showed a dramatic decrease in catalyst activity compared to the corresponding nonsonicated solutions, while presonication under methane led to only a small decrease in activity (see Figures 2 and 3). Addition of the
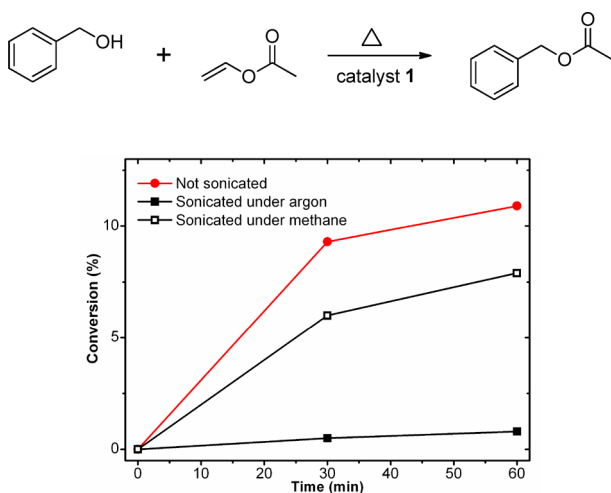

Figure 2. Time−conversion plot showing the effect of reaction mixture pretreatment by ultrasound for the transesterification reaction of VAc with BnOH. Reaction conditions: presonication time = 20 min, concentration of **1** = 0.25 mM, and temperature = 50 °C.
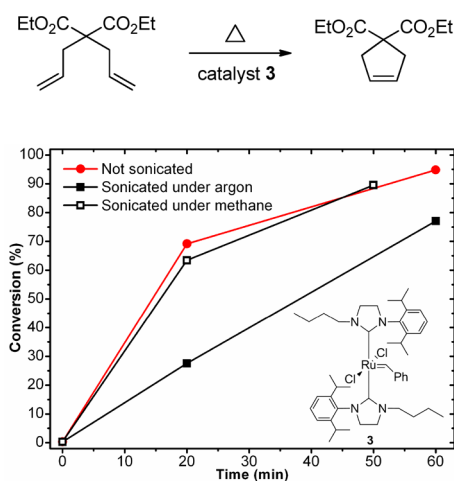

Figure 3. Time−conversion plot showing the effect of reaction mixture pretreatment by ultrasound for the ring-closing metathesis of DEDAM. Reaction conditions: presonication time = 75 min, concentration of model catalyst complex **3** = 0.60 mM with 300 equiv of DEDAM, and temperature = 75 °C.

radical scavengers BHT and BQ did not increase the activity under argon sonication of catalyst **2**,[14] whereas only a slight increase in conversion was observed when BHT was added to **1** (Supporting Information). This leads us to propose that deactivation is caused by a persistent species that is formed as a stable product of sonochemical reactions rather than the radicals themselves. Direct analysis of the sonicated solutions using GC-MS, GC-FID, and ^{1}H NMR, however, did not reveal the nature of this species.

It was possible to gain insight in the nature of the thermal impurities in an indirect way by carrying out acid−base titration experiments (Supporting Information). We chose thymol phthalein (TP) as the acid−base indicator. In its deprotonated form, TP is basic enough to react with very weak Brønsted acids (pH transition range 8.8−10.5).[22] Because free NHCs are very strong bases,[23] the possibility of deactivation of catalyst **1** by a weak acid should be taken into account. Dropwise addition of the standard transesterification reaction mixture, consisting of toluene, BnOH, and VAc (without catalyst **1**) to a solution of deprotonated TP in isopropanol showed unambiguously that the reaction mixture that was sonicated under argon contained three times more protic impurities than the freshly prepared or methane-sonicated reaction mixtures. Addition of the argon-sonicated reaction mixture to a solution of dimethyl yellow (DMY) indicator did not result in any observable color change. DMY has a color transition range at low pH values (2.9−4.0) and, therefore, the protic impurity must be a weak Brønsted acid. We propose that acetic acid is a likely candidate as it is a likely sonochemical degradation product of VAc. As a result of its high vapor pressure, VAc will be one of the main components of the cavitation bubble. In contrast, sonication of the metathesis reaction mixture (which contains toluene and less volatile DEDAM) under argon did not result in an appreciable formation of protic impurities. Brønsted acids are thus less of a concern for deactivation of the metathesis catalysts **2** and **3**;[24] instead, the formation of unsaturated hydrocarbons as well-established toluene pyrolysis products may be detrimental for this type of catalyst.[11b,25]

In conclusion, performance of sonochemically activated latent catalysts was shown to be reduced by persistent thermally produced impurities that deactivate the active catalyst. It was found that different sonochemical impurities are responsible for catalyst deactivation in both catalytic systems. Transesterification catalyst **1** is most likely deactivated by reaction with a weak Brønsted acid, whereas unsaturated hydrocarbons are the most likely cause of deactivation of metathesis catalysts **2** and **3**. Suppression of thermal effects by using methane as saturation gas significantly increased catalyst lifetime and, with that, catalyst performance in two different chemical transformations. Herewith, we have demonstrated that the suppression of thermal effects is of great importance in sonochemistry in cases where the product of mechanochemical scission is used in subsequent chemical processes, such as catalysis. Not only does this finding further confirm the true mechanochemical nature of catalyst activation, it also serves as an important guideline for future work involving sonochemically produced species.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and full characterization details of the polymers and catalyst complexes, as well as the results of scission kinetics, mechanocatalysis, and acid−base titration experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

BHT, 2,6-di-*tert*-butyl-4-methylphenol; BnAc, benzyl acetate; BnOH, benzyl alcohol; BQ, 1,4-benzoquinone; DEDAM, diethyl diallyl malonate; DMY, dimethyl yellow; FID, flame ionization detection; GC, gas chromatography; MS, mass spectrometry; NHC, *N*-heterocyclic carbene; NMR, nuclear magnetic resonance; PTHF, poly(tetrahydrofuran); RCM, ring-closing metathesis; TON, turnover number; TP, thymol phthalein; VAc, vinyl acetate

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(20) The concentration dependence of the mechanocatalyst activity is subject of a manuscript in preparation.

(21) In the mechanocatalytic tests using catalyst complex **1**, a pulsed sonication protocol was used which consisted of repeating "on/off" cycles at a pulse rate of 0.5 s "on", followed by 1.0 s "off" at 30% of the maximum amplitude.

(22) TP has a color change from blue to colorless, DMY changes from yellow to red upon lowering of the pH. For more information, see, for example, the Sigma-Aldrich website "Indicators for Non-Aqueous Titrations", http://www.sigmaaldrich.com/analytical-chromatography/analytical-products.html?TablePage=8680060 (accessed July 2012).

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■ NOTE ADDED AFTER ASAP PUBLICATION

Due to a production error, this paper was published on the Web on July 20, 2012, with minor text errors. The corrected version was reposted on July 23, 2012.