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## Mechanochemical reactions studied by *in situ* Raman spectroscopy: base catalysis in liquid-assisted grinding†

Martina Tireli,<sup>‡a</sup> Marina Juribašić Kulcsár,<sup>‡a</sup> Nikola Cindro,<sup>b</sup> Davor Gracin,<sup>a</sup> Nikola Biliškov,<sup>a</sup> Mladen Borovina,<sup>ab</sup> Manda Ćurić,<sup>a</sup> Ivan Halasz\*<sup>a</sup> and Krunoslav Užarević\*<sup>a</sup>

***In situ* Raman spectroscopy was employed to study the course of a mechanochemical nucleophilic substitution on a carbonyl group. We describe evidence of base catalysis, akin to catalysis in solution, achieved by liquid-assisted grinding.**

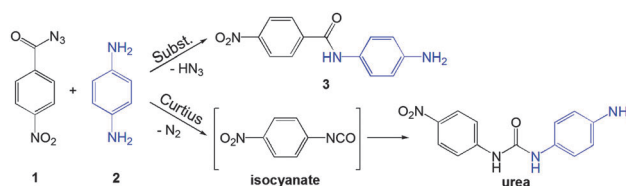
Organic synthesis is traditionally devoted to solution techniques for performing chemical reactions. However, solid-state reactions achieved by milling have emerged as an alternative to solution reactions.<sup>1–3</sup> Various organic reactions have been reported to occur under mechanochemical or solvent-free reaction conditions such as Suzuki<sup>4a</sup> and Sonogashira<sup>4b</sup> reactions, Michael addition,<sup>5a</sup> Diels–Alder reaction,<sup>5b</sup> including solid-state functionalization of graphene nanoplatelets,<sup>5c</sup> and Wittig reactions,<sup>5d</sup> as well as multi-step and one-pot reactions.<sup>6</sup> The scope of mechanochemical reactivity is significantly broadened by techniques such as liquid-assisted grinding (LAG)<sup>7</sup> where additives in sub-stoichiometric amounts have been found to improve the reactivity.<sup>8</sup> While the mechanism of their action is generally unknown, additives were found to act as catalysts<sup>9</sup> and may steer the reaction towards a specific product.<sup>10</sup> Also, it was recently indicated that a one-pot mechanochemical Gewald reaction can be catalysed by base.<sup>11</sup>

Contrary to well understood mechanisms of organic reactions in solution, mechanistic understanding of mechanochemical organic reactions has thus far remained elusive. This limits the use and applicability of these solid-state processes and their possible development for industrial purposes. Thus far, mechanisms of organic mechanochemical reactions were mainly deduced from stepwise *ex situ* analysis which provides only limited information due to an inherent time delay between sampling and analysis but also due to the fact that sampling may irreproducibly disturb the mechanochemical process.

Recently however, two techniques based on powder X-ray diffraction (PXRD)<sup>12</sup> or Raman spectroscopy<sup>13</sup> were introduced to study mechanochemical reactions *in situ* and in real time without the need to interrupt the milling process. The two techniques are complementary and are ideally employed simultaneously.<sup>14</sup> While PXRD is suitable for monitoring the evolution of bulk crystalline phases, Raman spectroscopy may be more appropriate for monitoring of amorphous or liquid phases which are particularly common in organic solid-state reactions.<sup>15</sup>

Here, we have employed *in situ* Raman spectroscopy to study the effect of additives on a mechanochemical organic reaction. Using the reaction between 4-nitrobenzoyl azide (1) and 1,4-diaminobenzene (2) yielding *N*-(4-aminophenyl)-4-nitrobenzamide (3) (Scheme 1) as a model nucleophilic substitution reaction on the carbonyl group, we have examined various additives differing in proticity, polarity and acid/base properties. Performed experiments aimed to establish whether the effect of additives is merely physical, through dissolution or enhanced molecular mobility,<sup>16</sup> or if the additives actively participate through chemical interactions.

Acyl azides are usually exploited in Curtius rearrangement where the acyl azide group rearranges to the isocyanate group upon exposure to mild external stimuli such as heat or irradiation. Curtius rearrangement during milling could be expected, based on the latest studies of energetics of mechanochemical treatment,<sup>17</sup> but the urea product that would result from the



**Scheme 1** Nucleophilic substitution on the carbonyl group of an acyl azide and potential Curtius rearrangement yielding an isocyanate intermediate which reacts with the amine to yield the urea derivative.

<sup>a</sup> Ruđer Bošković Institute, Bijenička 54, HR-10000 Zagreb, Croatia.  
E-mail: ivan.halasz@irb.hr, krunoslav.uzarevic@irb.hr

<sup>b</sup> Department of Chemistry, Faculty of Science, University of Zagreb,  
Horvatovac 102a, HR-10000 Zagreb, Croatia

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‡ These authors contributed equally to this work.



reaction of the amine with the isocyanate intermediate was not observed.<sup>18</sup> Instead, the azide here reacted with the amine to quantitatively yield the corresponding amide (Scheme 1). However, focus of this work is not mechanochemical formation of the amide group, for which other synthetic procedures under mechanochemical treatment were recently described,<sup>19</sup> but rather the mechanistic aspect of nucleophilic attack on the carbonyl group.

Time-resolved Raman spectra recorded *in situ* during milling (Fig. 1) were evaluated using two-dimensional (2D) correlation analysis according to the procedure described by Noda and Ozaki.<sup>20</sup> Both the synchronous and asynchronous spectra of all investigated systems exhibited stark similarities (Fig. S6–S9 in ESI†). Namely, both the diagonal and cross bands behave in the same way, which allows direct comparison of reactions under different reaction conditions. Assignment of the most relevant spectral features was done according to calculated Raman spectra<sup>21</sup> (Fig. 2) and previously published spectra of **2**<sup>22</sup> and compounds similar to **1**<sup>23</sup> (Table S1 in the ESI†). Formation of **3** in Fig. 1 is characterised by changes in the region between *ca.* 1600 and 1700  $\text{cm}^{-1}$  where it has three partially overlapping bands (Fig. 2). The amide II band at 1525  $\text{cm}^{-1}$  and the amide III band at 1268  $\text{cm}^{-1}$  emerge while the azide carbonyl stretching band at 1694  $\text{cm}^{-1}$  diminishes during milling. The band belonging to symmetric nitro group vibration at 1352  $\text{cm}^{-1}$  remains unaltered during the reaction. Curtius rearrangement would here result in 4-nitrophenyl isocyanate as an intermediate which would subsequently yield a derivative of urea (Scheme 1). The characteristic  $\nu(\text{CN})$  band of isocyanate expected at 2320  $\text{cm}^{-1}$  was, however, not observed (Fig. S10 in the ESI†).

The intensity of the band at 1239  $\text{cm}^{-1}$ , assigned to symmetric stretching of the azide group, initially decreases during milling but does not diminish completely (Fig. S11 in the ESI†). Simultaneously, the band at 1175  $\text{cm}^{-1}$ , which changes its position during milling to 1182  $\text{cm}^{-1}$  (Fig. 2b), and the band at 1266  $\text{cm}^{-1}$  increase in intensity, reflecting the formation of **3**. These bands are positively correlated in 2D synchronous spectra, but their correlation with the band at 1239  $\text{cm}^{-1}$  is absent (Fig. S6–S9 in the ESI†). However, cross peaks in asynchronous spectra show that the change in the 1239  $\text{cm}^{-1}$  band occurs before changes in bands at 1175 and 1266  $\text{cm}^{-1}$ . Interestingly, the intensity of the 2136  $\text{cm}^{-1}$  band, which is the antisymmetric counterpart of the 1239  $\text{cm}^{-1}$  band, continuously drops during the reaction. This indicates another emerging species contributing to the intensity of the band at 1239  $\text{cm}^{-1}$ . At first sight, no evidence could be found for the formation of hydrazoic acid ( $\text{HN}_3$ ) which is formally the leaving group in the substitution reaction (Scheme 1). This could have been explained by its volatility and possible degradation resulting from mechanical shock from milling ball impacts.<sup>24</sup> However, we note that the band at 1239  $\text{cm}^{-1}$ , which survives the whole milling process, could tentatively belong to  $\text{HN}_3$ , supporting the assumed reaction pathway toward amide without intermediate species, where  $\text{HN}_3$  is formed as a by-product.

Neat milling<sup>25</sup> of **1** and **2** for 60 minutes resulted in slow and incomplete formation of **3** (Fig. S12 in the ESI†). Liquid-assisted

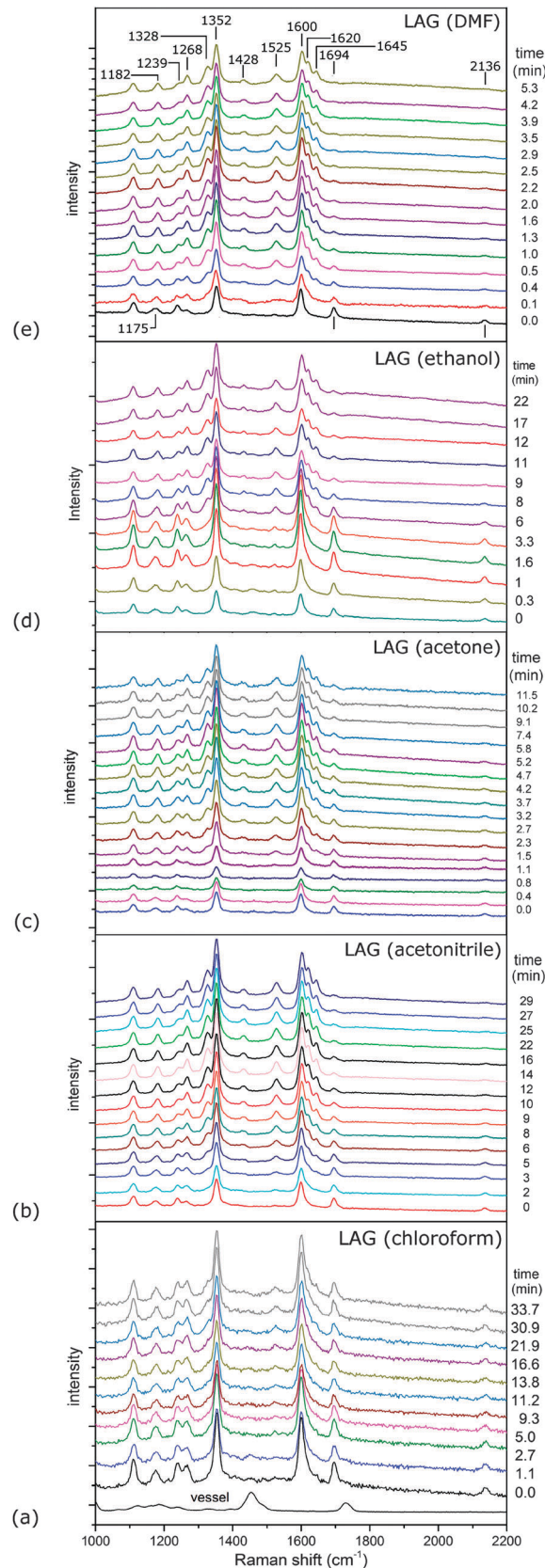


Fig. 1 Time-resolved Raman spectra recorded under different LAG conditions using as liquid additives: (a) chloroform, (b) acetonitrile, (c) acetone, (d) ethanol and (e) *N,N*-dimethylformamide (DMF). The spectrum of the reaction vessel is given in (a). Band positions are depicted in (e).



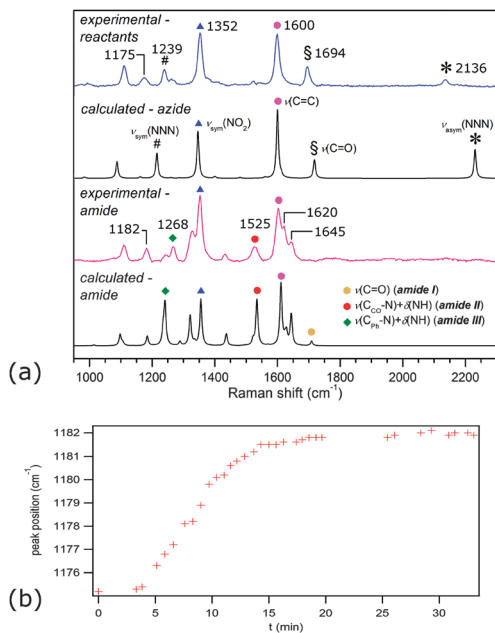


Fig. 2 (a) Observed and calculated Raman spectra of participating species with band positions and assignments. Raman scattering of the amine was very weak in comparison to scattering of azide and amide. (b) Band shift during LAG reaction with acetonitrile.

grinding was, in comparison, far more successful in driving the amide formation (Fig. 1, Table 1). Except for chloroform which had little effect, liquid additives dramatically increased the reaction rate. This was especially true for LAG using DMF, followed by ethanol, acetone and acetonitrile. As stated above, all studied reactions proceeded along the same pathway, thus allowing examination of the effect of additives on the mechanochemical process. Since LAG with chloroform resulted in no or only minor reaction rate acceleration, while with other protic and polar liquid additives significantly accelerated the reaction, we conclude that the mere presence of the liquid to enhance the molecular mobility was not enough to facilitate product formation. This is also evident from the lack of a correlation

Table 1 Reaction times using various additives and their properties

	Reaction time (min)	Basicity (DN) <sup>a</sup>	Dipole moment ( <i>D</i> )	Relative permittivity
LAG (liquid)				
DMF	4	26.6	3.82	36.1
Ethanol	8	19.2	1.69	24.5
Acetone	10	17.0	2.88	20.7
Acetonitrile	16.5	14.1	3.92	38.0
Chloroform	30 <sup>b</sup>	—	1.15	4.81
No liquid	60 <sup>b</sup>	—	—	—
ILAG (ethanol, salt)				
dabco <sup>c</sup>	6.5	— <sup>d</sup>	—	—
NaOAc	7.2	— <sup>d</sup>	—	—
NH <sub>4</sub> NO <sub>3</sub>	8	— <sup>d</sup>	—	—

<sup>a</sup> DN – donor number by Gutmann.<sup>26</sup> <sup>b</sup> Reaction was not complete. <sup>c</sup> dabco is not a salt but a molecular compound. <sup>d</sup> We worked under the assumption that dabco and NaOAc increased the basicity while ammonium nitrate reduced the basicity relative to pure ethanol.

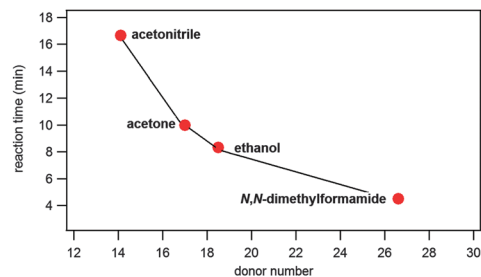


Fig. 3 Correlation of reaction times and liquid basicity, expressed through Gutmann's donor numbers,<sup>26</sup> in LAG reactions.

between solubilities of participating species (Table S2 in the ESI<sup>†</sup>) in each solvent and the corresponding reaction times.

However, we note that product formation was faster when the liquid additive was more basic. This is clearly suggested from the correlation of the time needed for reaction completion and basicity of the liquid additive described using Gutmann's donor numbers<sup>26</sup> (Table 1, Fig. 3). Such a correlation with reaction times could not be established using liquid's polarity, represented by the molecule dipole moment, or its relative permittivity (Table 1).

To corroborate this, simple salts were introduced in the reaction mixture along with ethanol (Table S1 and Fig. S13–S15 in the ESI<sup>†</sup>). Resulting reaction conditions are termed ion- and liquid-assisted grinding (ILAG) and may offer further possibilities of reaction control.<sup>10b</sup> With basic sodium acetate (10 mol% with respect to reactants) added along with ethanol, the reaction was accelerated relative to pure LAG with ethanol. If an even stronger base like 1,4-diazabicyclo[2.2.2]octane (dabco) was used in an analogous experiment, the reaction was even more accelerated. If however, slightly acidic ammonium nitrate was added along with ethanol, the reaction rate remained essentially the same. This strongly supports the conclusion that this nucleophilic substitution reaction on a carbonyl group is base-catalysed and that proton abstraction is an important step in the reaction's mechanism.

In summary, we have employed *in situ* Raman spectroscopy for uninterrupted, real-time monitoring of a mechanochemical organic reaction. Nucleophilic substitution on the carbonyl group was conducted under various LAG conditions which revealed that the reaction is base-catalysed by the liquid additive. Such behaviour resembles acid/base catalysis as could be expected for solution reactions and indicates the possibility of reaction transfer to the liquid phase under LAG conditions.<sup>7c,27</sup> The presented results not only demonstrate high sensitivity of organic mechanochemical reactions to additives, but also provide a new entry for systematic understanding and control of mechanochemical reactivity.

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- 25 Mechanochemical reactions were carried out using a Retsch MM301 ball mill operating at 30 Hz and in-house manufactured 14 mL transparent poly(methylmethacrylate) (PMMA) milling vessels with two 7 mm diameter stainless steel balls (ball weight 1.3 g). For each experiment, 266 mg (1.38 mmol) azide and 150 mg (1.38 mmol) amine were directly weighed to one half of the reaction vessel. The other half was filled with grinding balls and 75  $\mu\text{L}$  of the liquid additive giving the same ratio of liquid volume to mass of solid reactants ( $\eta$ ) in all experiments,  $\eta = 0.18 \mu\text{L mg}^{-1}$ . The two halves of the jar were carefully joined together so that the solids did not mix with the liquid before milling was initiated. *In situ* monitoring was performed as described before using a portable Raman spectrometer<sup>13</sup> with a PD-LD LS2 laser source (784 nm). Scattered radiation was analysed using an Oceanoptics Maya2000 Pro spectrometer. The Raman probe for the laser was positioned below the milling vessel for data collection. Each spectrum was typically collected for 10 seconds. The PMMA vessel contribution to the collected Raman spectra was subtracted. Products were characterized by <sup>1</sup>H and <sup>13</sup>C NMR and infrared spectroscopy (Fig. S1–S4 in the ESI†) as well as by PXRD (Fig. S16 in the ESI†).
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