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► **To cite this version:**

Paulo F. M. Oliveira, Michel Baron, Alain Chamayou, Michel Baltas, Brigitte Guidetti, et al.. Lowering the Activation Energy under Mechanochemical Conditions: The Case of 2,3-diphenylquinoxaline. *ChemistrySelect*, 2016, 1 (5), p. 984-988. 10.1002/slct.201600127 . hal-01620288

HAL Id: hal-01620288

<https://hal.science/hal-01620288v1>

Submitted on 8 Nov 2019

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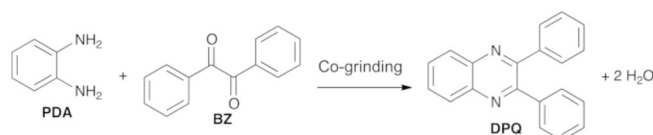
Lowering the Activation Energy under Mechanochemical Conditions: The Case of 2,3-diphenylquinoxaline

Paulo F. M. Oliveira,^{*,[a, b]} Michel Baron,^{*,[a]} Alain Chamayou,^[a] Michel Baltas,^[b] Brigitte Guidetti,^[b] Naoki Haruta,^[c] Kazuyoshi Tanaka,^[c] and Tohru Sato^{*,[c, d]}

The kinetics of 2,3-diphenylquinoxaline synthesis was investigated in mechanochemical conditions aiming to estimate the overall activation energy. Arrhenius plot revealed a change in the activation energy around the eutectic melting of the powder mixture under mechanical activation. Below this transition zone the reaction between solids prevails, where the mechanical effects lower the activation energy. Above it, part of the energy is used to induce the eutectic, and the apparent activation energy is higher. DFT calculations showed a reaction barrier similar to the experimental one for higher temperatures. This study is the first that demonstrates the effect of mechanical energy to lower an activation barrier for ball milled organic reaction.

Inducing transformations upon directly milling or grinding solid reactants became recently an important tool in organic chemistry, offering an innovative sustainable way for organic syntheses.^[1] Despite the ongoing progress on organic mechanochemistry in the preparation of fine chemicals,^[2-5] little is discussed and developed about the kinetics of such systems^[6] when compared to inorganic ones.^[7] The present article reports the first attempt to estimate the activation energy from kinetic experimental data of a mechanically induced reaction between organic solid reactants in a vibratory ball mill, which revealed thermally and mechanically influenced domains.

The mechanically induced 2,3-diphenylquinoxaline (DPQ) synthesis (Scheme 1) was investigated. The reaction was carried out between solid *o*-phenylenediamine (PDA) and benzil (BZ) in stoichiometric conditions. The effects of milling temperature



Scheme 1. Synthesis of 2,3-diphenylquinoxaline (DPQ) by co-grinding.

(T_m) and of the weight of the milling ball (m_{MB}) were evaluated. For this purpose, the milling device Pulverisette 0 (P0, Fritsch) was equipped with a temperature equilibrating system (Fig. S2 in Supporting Information). Six different T_m were studied ranging from 12 °C to 35 °C for two different m_{MB} weights, 132 g and 507 g, keeping the other reaction conditions constant, including the reactants ratio (1:1 mol/mol) (See Supporting Information for experimental details). The kinetic curves of DPQ synthesis are presented in Figure 1 at $T_m = 21$ °C and follow an

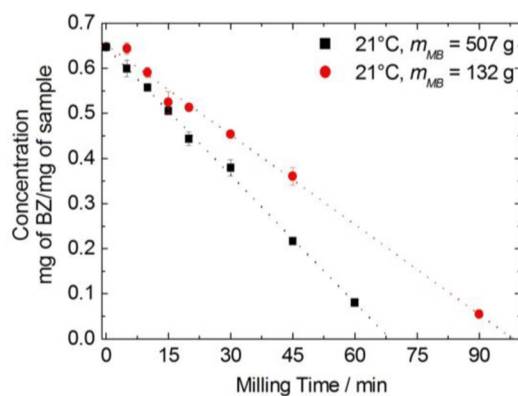


Figure 1. Kinetic monitoring of BZ transformation for DPQ synthesis at 21 °C for different m_{MB} .

apparent zero-order reaction type, as reported previously for other solid-state and mechanochemical reactions.^[6c-d,7e]

This zero-order pattern in is a result of an overall process accounting for both chemical and physical rates.^[7e,8] However, the continuous milling provides surface cleaning and exposure, allowing the prompt replacement of species created by reaction at the solid surfaces.^[9] Therefore, the milling and mixing actions limit diffusion and mass-transfer influences^[9] and the re-

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Table 1. Rate constants for zero-order kinetic model as function of milling temperature (T_m) and weight of the milling ball (m_{MB}).		
T_m (°C)	k (s ⁻¹) (m_{MB} = 132 g)	k (s ⁻¹) (m_{MB} = 507 g)
12	$(7.34 \pm 0.12) \times 10^{-5}$	$(1.29 \pm 0.05) \times 10^{-4}$
16	$(8.88 \pm 0.10) \times 10^{-5}$	$(1.41 \pm 0.08) \times 10^{-4}$
21	$(1.11 \pm 0.09) \times 10^{-4}$	$(1.57 \pm 0.04) \times 10^{-4}$
27	$(1.72 \pm 0.11) \times 10^{-4}$	$(1.81 \pm 0.31) \times 10^{-4}$
32	$(2.59 \pm 0.01) \times 10^{-4}$	$(3.39 \pm 0.21) \times 10^{-4}$
35	$(3.10 \pm 0.03) \times 10^{-4}$	$(4.68 \pm 0.44) \times 10^{-4}$

Arrhenius plot was constructed with the experimental data of DPQ synthesis in order to estimate the activation energies in the experimental conditions (Figure 2). In these studies, the temperature T in these equations was represented by the milling temperature T_m .

action rate should represent mostly the chemical rate in this case of low molecular mass compounds. Consequently, as the chemical reaction is induced by milling, the constant reaction rate can be the result of the evenly distributed over time application of the mechanical energy through the single ball.

As shown in Figure 1, in stoichiometric conditions, the reaction follows an apparent zero-order model. In such cases, the rate law is represented as follows:

$$\frac{dC}{dt} = -k \quad (1)$$

The concentration C of benzil (or *o*-phenylenediamine) at a time t is a direct product of the overall rate constant k , which varies as function of the milling temperature.

The overall rate constants as function of T_m and m_{MB} are displayed in Table 1. The values of k were determined from the graphics of C (mg/mg) versus t (min) for each condition with at least two independent runs, as for 21 °C in Figure 1 (Fig. S3 in Supporting Information for other T_m). The milling temperatures indicated in Table 1 was reached after 12 h stabilization.

The rate constant increases when T_m increases revealing the sensitivity of the ball-milled powder mixture to temperature changes (Table 1). The same is observed for the m_{MB} . The heavier 507 g ball induces faster reaction than the 132 g ball for the same T_m .

By using the rate constants from Table 1 the apparent activation energy for DPQ mechanosynthesis was estimated. Arrhenius equation (2) is the most used to describe the temperature dependence of reaction rate constant also for solid-state reactions.^[10]

$$k = Ae^{-\frac{E_a}{RT}} \quad (2)$$

In the equation above, E_a is the activation energy, A is the frequency or pre-exponential factor and R is universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). The kinetic parameters can be determined graphically from the Arrhenius plot, by using the reaction rate constants obtained at different temperatures and the Arrhenius equation in the linear form (3). The slope on the curve $\ln(k)$ versus the reciprocal of temperature $1/T$ gives the E_a/R and the intercept the $\ln A$.

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (3)$$

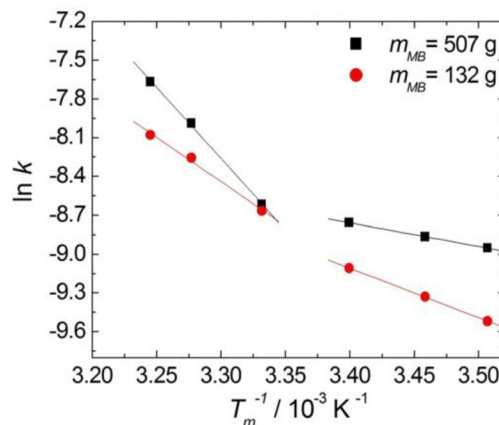


Figure 2. Arrhenius plot from the rate constants and the milling temperature (T_m) for DPQ synthesis in P0 with different weights of the balls (m_{MB}).

Surprisingly, the expected linearity for Arrhenius plot was not observed in DPQ synthesis (Figure 2), but two linear regions were identified instead. The deviations from linearity indicate the variation of activation energy, attributed to changes in the reaction mechanism and/or in the rate-determining step. This was also discussed for other condensed phases reactions that used Arrhenius equation to estimate the activation energy.^[11] Furthermore, unlike the homogenous systems, the physical properties of solid reactants (or their mixtures), can evolve during reaction, which directly affects the kinetics of such reactions. In these cases, phase transitions (amorphization or polymorphism)^[12] and eutectic melting^[13] are often reported.

DSC and XRD were carried out to study the behavior of the powder mixture.^[14] The analyses of the pure reactants, PDA and BZ, before and after milling did not reveal any amorphization or polymorphic transition. However, DSC measurements of the equimolar powder mixture showed an endothermic peak at 77 °C (See Fig. S4 in Supporting Information), while the melting point of BZ and PDA are respectively 94 °C and 101 °C. A hot-stage microscopy was adapted, in which the melt of the two crystals at their contact interface was observed starting at 48–50 °C and progressing to the bulk (Figure 3). This reveals the highly eutectic forming character of the BZ:PDA mixtures.

Therefore, considering that the mechanical energy is capable of lowering the temperature to form the eutectic melting, this mechanically induced phase-change can be responsible for the change in the activation energy observed in Arrhenius plot.

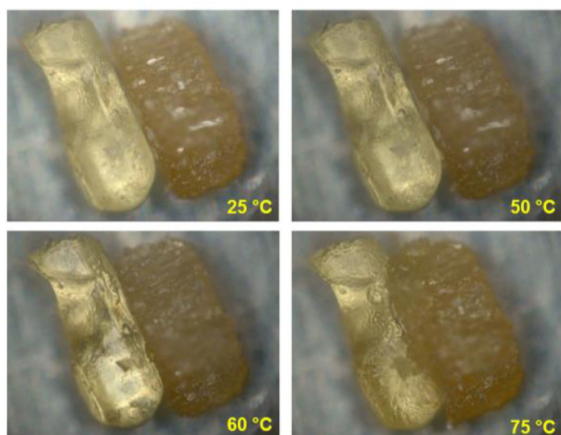


Figure 3. Hot-stage microscopy with BZ (yellow crystal) and PDA (brown crystal). From 50 °C some melt are observed on the solid-solid interface.

Regarding the formation of a fluid phase by the mutual action of milling and temperature above 27 °C, the kinetic parameters were estimated for each range of linearity, above and below 27 °C, for the two different m_{MB} , utilizing the linear fit from Equation (2). Table 2 summarizes the calculated kinetic parameters E_a and $\ln A$ for Arrhenius equation.

T_m (°C)	m_{MB} (g)	E_a (kJ mol ⁻¹)	$\ln A$
12 – 21	132	31.87	3.92
	507	15.19	-2.54
27 – 35	132	57.07	14.21
	507	91.89	28.21

Concerning Arrhenius kinetic parameters, the activation energy below 27 °C is 31.9 kJ mol⁻¹ and 16.0 kJ mol⁻¹ for 132 g and 507 g m_{MB} respectively. These values are lower than expected for typical organic reactions that generally present E_a of 40–200 kJ mol⁻¹.^[15] At lower temperatures the chemical kinetics is supposed to be rate determining and, therefore, these lower values of E_a can be a result of the mechanical action lowering the activation energy and accelerating the chemical kinetics. This effect is confirmed by the role of m_{MB} , the heavier ball reducing the overall energy barrier more than the lighter one. Some authors pointed out the role of mechanical action in lowering the activation barrier for transformation in the field of mineral or metallic materials.^[16–20] This can be the case for the DPQ synthesis at lower temperatures in the experimental conditions, where ballistic effects are more significant than thermal ones.^[12,21]

The second range of temperature is characterized by a change in the activation energy due to the mechanically induced phase-changing above 27 °C. In this domain, an opposite effect as function of the m_{MB} is observed with $E_a=57.1$ kJ/mol for $m_{MB}=132$ g and 91.9 kJ/mol for $m_{MB}=507$ g, because

the higher the energy of mechanical interaction more powder undergoes the transformation, resulting in more eutectic melting formation.

As such phase is fluid, the chemical species react as in solution-based media presenting higher activation energy values typical for organic chemical reactions in classical systems.^[15] This explains why the 132 g ball leads to a lower overall E_a . The lighter ball induces only a small part of reactive eutectic and then, the major part of the mixture continues to react as solids. Figure 4 illustrates and summarizes the stages of the discussion above as function of T_m and m_{MB} .

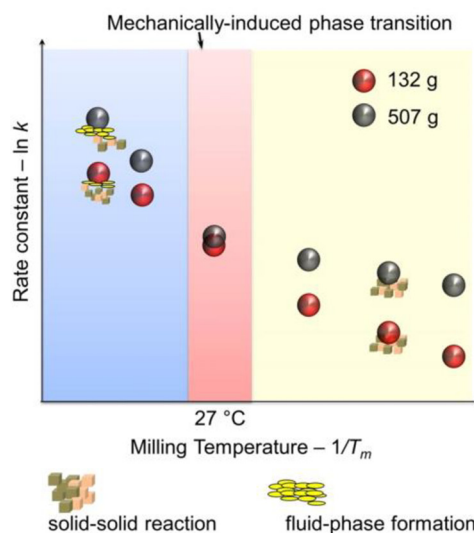


Figure 4. Proposed scheme of reaction rate for mechanically induced DPQ synthesis as function of milling temperature and weight of the milling ball in vibratory ball-mill P0. Below 27 °C solid-solid reaction predominates and above 27 °C, a phase-changing occurs due to mechanical stress events.

DFT calculations were performed to give a supplementary insight on the differences of activation barriers and mechanistic understandings. In the reaction yielding DPQ, BZ should take a preferable *cis* conformation as shown in Figure 5. The *trans*-

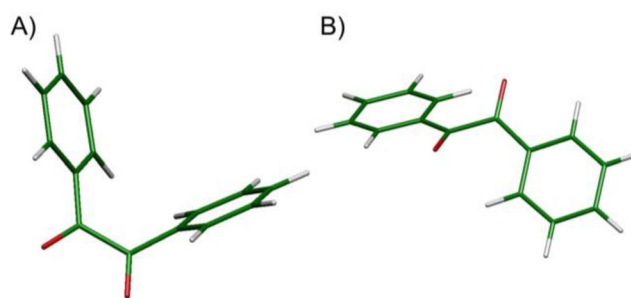


Figure 5. Optimized structures of benzil (BZ) conformers: A) *cis* and B) *trans*. The B3LYP/6-311G(d,p) level of theory was used with Gaussian 09.^[22] The *cis* conformer has C_1 symmetry, whereas the *trans* conformer has C_2 symmetry. The *cis* conformer has one vibrational mode with the imaginary frequency of 16i cm⁻¹.

formation from the stable *trans* conformer to the *cis* conformer can be achieved by both mechanisms, mechanical and thermal paths, requiring $70.38 \text{ kJ mol}^{-1}$ for conversion. The *cis* conformer has one vibrational mode with the imaginary frequency of $16i \text{ cm}^{-1}$. This means that the present reaction is not an elementary process but consists of some processes.

To explain the two different slopes observed in the Arrhenius plots, it is assumed that the overall rate constant k is a sum of a temperature-independent rate constant k_0 which is attributed to the mechanical path and a temperature-dependent term k_{th} which describes the thermally excited mechanism:

$$k = k_0 + k_{th} \quad (4)$$

$$k_{th} = A \exp\left(-\frac{E_a}{RT_m}\right) \quad (5)$$

The model functions Eqs. (4) and (5) were fitted to the experimental data. The result is shown in Figure 6 and the fitted

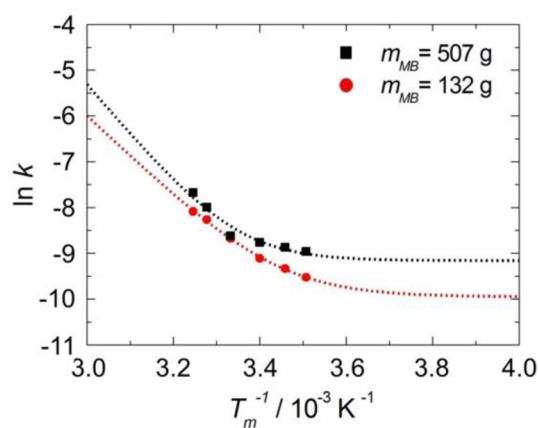


Figure 6. Curve fitting for the Arrhenius plot with the experimental rate constants (circle and square) k and milling temperatures T_m . The employed model function is defined by Equations (4) and (5). The obtained parameters, k_0 , $\ln A$, and E_a are listed in Table 3.

parameters, k_0 , $\ln A$, and E_a displayed in Table 3. It is seen that

m_{MB} (g)	k_0 (s^{-1})	$\ln A$	E_a (kJ mol^{-1})
132	4.80×10^{-5}	21.06	75.02
507	1.06×10^{-4}	28.21	92.95

the mechanical rate constant k_0 with a 507 g ball is larger than that with a 132 g one. This is because the heavier ball can give larger mechanical energy to overcome the reaction barrier. The overall activation energies of the reaction obtained from the fittings are higher than 75 kJ mol^{-1} , which is consistent with DFT calculations that indicated that these energies should be

higher than the energy for *trans* to *cis* conformer conversion ($70.38 \text{ kJ mol}^{-1}$).

Typically, the modeling and DFT calculation describes the reaction between mobile species such as in gaseous or liquid media. Compared to the experimental results, it is more likely the case above 27°C , that is, the reaction in the induced eutectic melting with highest activation energies. Since the experimental values from Table 2 ($91.89 \text{ kJ mol}^{-1}$) and Table 3 ($92.95 \text{ kJ mol}^{-1}$) for $m_{MB} = 507 \text{ g}$ converge, it reinforces the attribution to a fluid phase formation induced by mechanical energy for T_m above 27°C . The lower milling intensity induces smaller quantities of eutectic melting and the mechanical energy continues to act by lowering the overall activation barrier for reaction in the solid fraction. This also explains the difference of less 18 kJ mol^{-1} for 132 g ball compared to the 507 g one, obtained from modeling.

The contribution of the solid state itself in decreasing the reaction activation barrier must also be highlighted. The proximity of the reactive sites and the deformation induced by the mechanical action allows to figure a case of particular reaction pathways with the proximity of the (bonding and antibonding) orbitals.^[23]

In conclusion, the first study allowing the estimation of the overall activation energy for an organic reaction in ball mill is reported. The DPQ synthesis was investigated and revealed the variation of the overall activation energy as function of milling temperature and intensity. In mechanochemical conditions where the mechanical effects prevail, the E_a was lower than expected when compared to typical values of thermally activated reactions. At higher temperature the mechanical energy displaces the eutectic melting, resulting in higher E_a as for fluid systems. In sum, the estimated values of apparent activation barriers reported in this paper demonstrated that the mechanical energy is capable of lowering the overall reactions barriers in organic mechanochemistry. The established correlation between experiments and the modeling validates the original approach of the estimation of activation barriers for mechanochemical organic reactions.

Supporting Information

Experimental details, including synthetic procedure and the milling device description are given in the Supporting Information. Kinetic curves at different milling temperatures, DSC and characterization data of 2,3-diphenylquinoxaline are also included.

Acknowledgements

The authors acknowledge the CNRS/JSPS France-Japan joint research project ($n^\circ \text{ PRC0709}$, 2013–2014) for financial support, Isabelle Fabing for HPLC method development, Sylvie Delconfetto for DSC measurements, Bruno Boyer for the experimental apparatus adaptation and Grazielle Aguiar for experimental support. Numerical calculations were partly performed at the Supercomputer Laboratory of Kyoto University and the Research Center for Computational Science, Okazaki, Japan.

Keywords: Mechanochemistry · Kinetics · Activation energy · Computational chemistry · Green chemistry

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