Mechanochemistry

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Probing Force with Mechanobase-Induced Chemiluminescence

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Abstract: *Mechanophores capable of releasing N-heterocyclic carbene (NHC), a strong base, are combined with triggerable chemiluminescent substrates to give a novel system for mechanically induced chemiluminescence. The mechanophores are palladium bis-NHC complexes, centrally incorporated in poly(tetrahydrofuran) (pTHF). Chemiluminescence is induced from two substrates, adamantyl phenol dioxetane (APD) and a coumaranone derivative, upon sonication of dilute solutions of the polymer complex and either APD or the coumaranone. Control experiments with a low molecular weight Pd complex showed no significant activation and the molecular weight dependence of the coumaranone emission supports the mechanical origin of the activation. The development of this system is a first step towards mechanoluminescence at lower force thresholds and catalytic mechanoluminescence.*

Developing molecular force probes for the high-sensitivity detection of small forces would enable the study of a broad array of mechanical phenomena, particularly in soft materials and biological systems. In the past decade, polymer mechanochemistry has opened up many new mechanoresponsive behaviors,[1–5] of which mechanically induced fluorescence[6,7] and mechanoluminescence[8] have emerged as valuable indicators for stress in polymeric materials. Whilst the former is now a highly established force-sensitive transformation,[7,9–11] mechanoluminescence is preferred in situations where sensitivity and time resolution are critical, as no excitation signal is required to visualize the signal and light is emitted directly on bond scission. The analytical scope of mechanoluminescence now spans a wide range of polymers, from common engineering materials such as polyacrylates and thermoplastic elastomers[12] to novel designer systems, including multiple interpenetrating network elastomers[13] and supramolecularly cross-linked gels.[14]

Despite this progress, only one luminescent mechanophore has been developed to date, bis(adamantyl)dioxetane, and its mechanical reactivity is ultimately determined by the strength of the dioxetane bond, which has an activation energy barrier to decomposition of approximately $150\,\mathrm{kJ\,mol^{-1}}$ (at zero force).[15] It would be desirable to lower the force threshold at which mechanoluminescence is activated, in part so that mechanical processes operative at lower forces may be characterized. However, direct synthetic modification of the dioxetane structure is far from trivial: thermally more labile dioxetanes are generally more difficult to synthesize and may not necessarily be mechanically more labile.

We set out to develop an alternative approach to mechanoluminescence that obviates the need for complex synthetic modification of the dioxetane mechanophore. The rich array of existing substrates for highly efficient, chemically triggerable chemiluminescence served as our source of inspiration.[16] We envisaged that it would be possible to activate such substrates mechanochemically. In the course of our research, complexes of transition metals and polymers end-functionalized with N-heterocyclic carbene ligands have proven to be excellent latent sources of carbenes,[4,5,17] which are both highly basic and nucleophilic. In the present work we make use of their high basicity to deprotonate a substrate. The primary advantage of such a system, in which the mechanophore is decoupled from the chemiluminescent emission, is that transition-metal complexes with thermal stabilities similar to weak covalent bonds are expected to have lower stability under force by virtue of the longer C—M bond with a wider potential well.[18] This prediction can be rationalized by representing force with a "tilted potential energy surface", on which the barrier for scission of the bond with the wider potential well decreases more with applied force. Additionally, much higher quantum yields are achievable with the precursor chemiluminescent substrates than with alkyl-substituted dioxetanes such as the bis(adamantyl)dioxetane,[16,19] boosting sensitivity.

To test the generality of the concept, we selected two different chemiluminescent probes (Scheme 1): a spiroadamantyl-substituted phenolic 1,2-dioxetane, 3-(4-methoxyspiro[1,2-dioxetane-3,2′-tricyclo[3.3.1.13,7]decan]-4-yl)phenol **1**,[20,21] and a 2-coumaranone derivative, ethyl (5-fluoro-2-oxo-2,3-dihydrobenzofuran-3-yl) carbamate **2**.[22,23] When exposed to a chemical base as stimulus, both substrates form a high-energy intermediate which gives out light upon decomposition under ambient conditions. In the case of **1**, deprotonation of the phenol group affords an unstable intermediate dioxetane[24] that decomposes within minutes (by comparison, the TBDMS-protected derivative of the phenol has a half-life of 4 years)[25] with the concomitant emission of blue light with a high excitation yield (total quantum yield 12% in acetonitrile).[26] Chemiluminescence of the other probe, coumaranone **2**, is triggered by deprotonation of the lactone at the α-position. Subsequent reaction with oxygen generates an unstable dioxetanone intermediate in situ, which decomposes to give out bright blue light.[27]

Metal NHC complexes are well-known as thermally latent catalysts and bases.[28] Our group has reported on the use of silver(I) and ruthenium(II) bis-NHC complexes centrally

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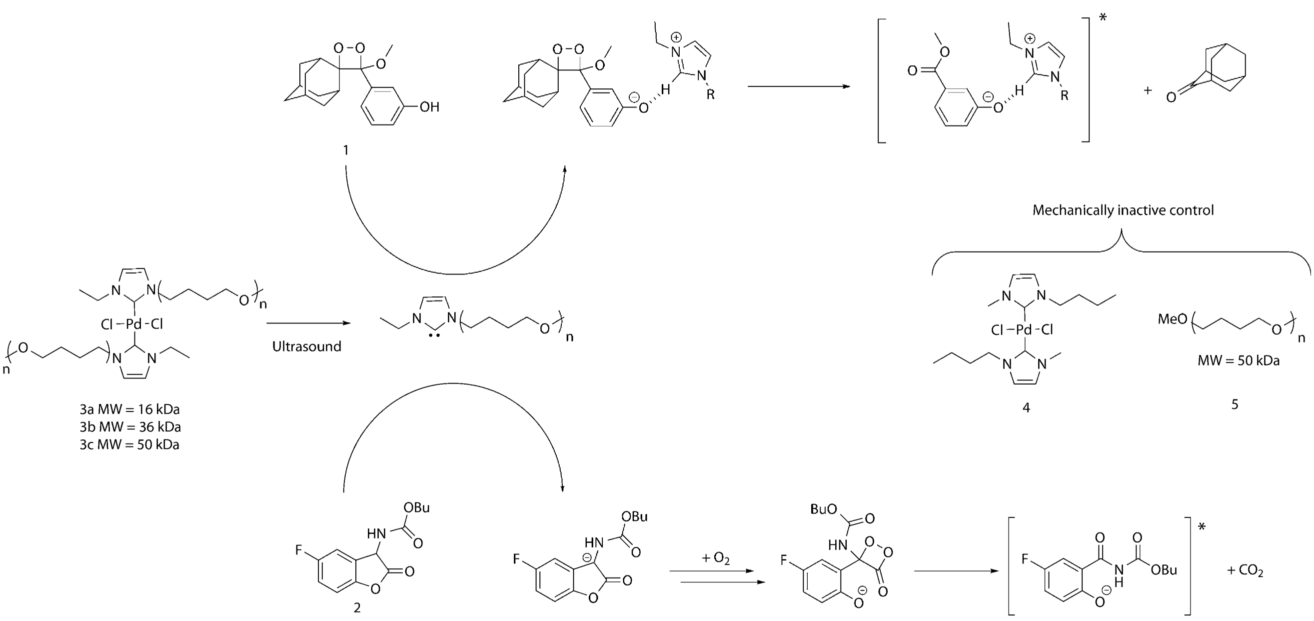

Scheme 1. Scission of palladium-NHC coordination polymer, producing free carbene **3**; the carbene deprotonates substrate **1** or **2**, initiating chemiluminescent decomposition. **2** requires the presence of oxygen to generate an unstable dioxetanone. Sonicating **1** or **2** in the presence of **4** and **5** is used as a non-mechanical control.

incorporated in poly(tetrahydrofuran) (pTHF) as mechanically latent catalysts for transesterification[29] and metathesis[5,30] reactions. The study at hand makes use of newly developed palladium bis-NHC complexes **3a–c**, which exhibit greater thermal stability than the silver complexes.[31,32] Despite their thermal stability, palladium bis-NHC complexes are highly susceptible to mechanochemical scission. The complex with the highest molecular weight studied, **3c** (weight-average molecular weight 50 kDa) decomposed with a scission rate constant of $1.0\times10^{-3}\,s^{-1}$ upon continuous sonication under air in toluene, as determined by analysis of GPC traces from aliquots taken at regular intervals from the sonicated solution. On lowering the molecular weight to 16 kDa, as in **3a**, the rate constant decreased to $8.3\times10^{-5}\,s^{-1}$ (Figure 1). Plotting the rate constants measured under these conditions against molecular weight gave a low limiting molecular weight for mechanochemical chain scission of **3** of about 13 kDa (Supporting Information, Figure S4).

To obtain mechanically induced chemiluminescence, the palladium complexes were first coupled with base-sensitive coumaranone **2**. Subjecting a toluene solution of mechanically active palladium bis-carbene polymer (50 kDa) **3c** (0.2 mM) and coumaranone **2** (2 mM) to continuous sonication under air led to the emission of light from the solution, which is faintly observable by eye in a darkened room. We followed the mechanoluminescence intensity in real time with a photodiode placed underneath the flask; the resulting time–intensity traces are shown in Figure 2. The intensity of the chemiluminescence reaches its maximum after a few minutes, before decaying over the course of approximately one hour. Support for the mechanochemical origin of the luminescent signal comes from experiments with **3a–c**, with increasing molecular weight of the complex. At identical molar concentrations of complex and chemiluminescent substrate, the maximum emission intensity increases with the molecular weight of the complex, reflecting molecular-weight-dependent scission rates established by GPC on the solutions (see Figure 1 and the Supporting Information). The higher scission rates compete better against recoordination of the NHC to palladium, providing a greater initial "burst" in the concentration of free carbene.

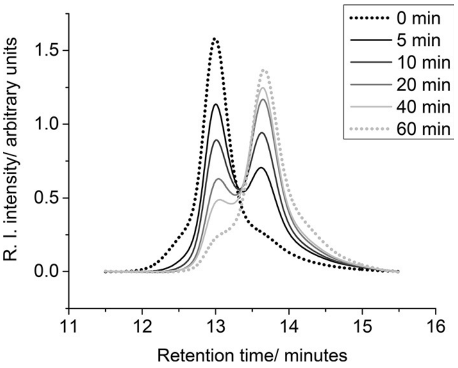

Figure 1. GPC traces of **3c** (initial weight-average $M_W = 50$ kDa; PDI = 1.2, black dotted line) subjected to continuous sonication under air for 60 minutes at 25 °C in toluene in the presence of coumaranone **2**. The GPC trace after one hour of sonication (light gray dotted line) indicates that the molecular weight has decreased to half the initial molecular weight, supporting scission at the centrally incorporated palladium complex.

In contrast to this, when we sonicated a solution in which polymeric **3** was replaced with small-molecule bis-NHC palladium complex **4** together with unfunctionalized pTHF **5**, only very weak background emission with a constant intensity was observed. Emission with similarly low intensity was observed when a blank toluene solution or toluene

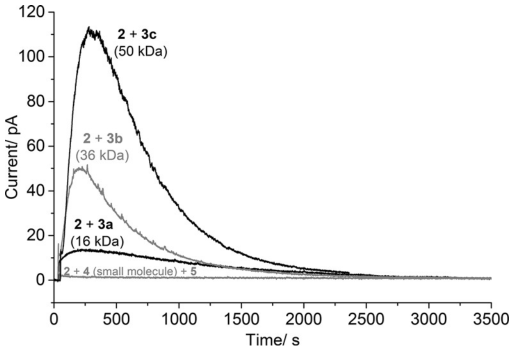

Figure 2. Time traces of light emission observed upon sonochemical activation of 0.2 mm solutions of palladium-NHC complexes **3a–c** or **4** and **5** in the presence of coumaranone **2** (2 mm) in air-saturated toluene at 25 °C. The light emission was recorded with a photodiode placed beneath the flask.

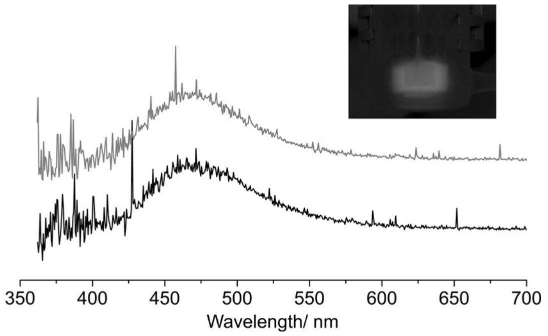

Figure 3. Normalized emission spectra of mechanoluminescence from adamantyl phenol dioxetane **1** (0.25 mm) initiated by mechanically liberated NHC from scission of **3c** (0.25 mm) (lower curve, black) and of chemiluminescence of **1** initiated by (non-mechanical) 1,8-diazabicycloundec-7-ene (DBU, 50 mm) (upper curve, gray). Both spectra were recorded in 1:1 toluene/acetonitrile, with an intensified CCD camera in combination with a spectrograph. Each spectrum represents the average of twenty sequentially recorded spectra. The spectra were corrected for the wavelength-dependent sensitivity of the detection system with a tungsten halogen source. Inset: photo of mechanoluminescence from **1** induced by mechanical scission of **3c** after 40 minutes of sonication, whilst still sonicating (a brief flash from an external light source was applied during the exposure to illuminate the set-up).

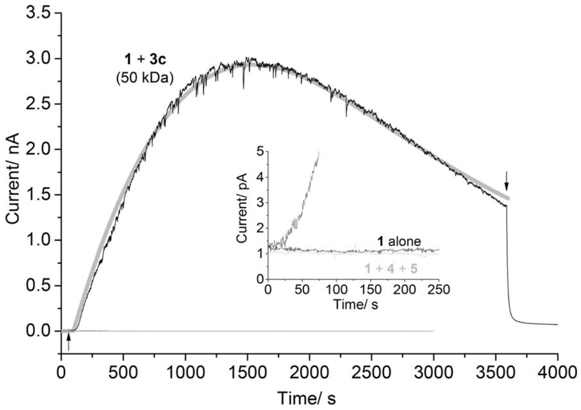

Figure 4. Time trace of light emission observed from **1** (0.25 mm) upon sonochemical activation of palladium-NHC complexes **3c** (0.25 mm) (black curve) in methane-saturated toluene:acetonitrile 1:1 ν/ν at 25 °C. Upward arrows and downward arrows indicate the start and end of sonication, respectively. The fit to the kinetic model (see the Supporting Information) is shown by the thick gray curve overlaying the experimental data. The inset shows the control experiments with **1** alone (black curve) or in the presence of **4** and **5** (gray curve), also in methane-saturated toluene/acetonitrile 1:1 ν/ν at 25 °C. The light emission was recorded with a photodiode placed beneath the flask.

solutions of coumaranone **2** alone were sonicated in the presence of air. We attribute this low intensity signal (which is approximately 100 times smaller than observed from sonicating coumaranone **2** in the presence of polymeric Pd-complex **3c**) to sonoluminescence,[33,34] and we conclude that the absence of signal above the background in the presence of low-molecular-weight **4** and unfunctionalized pTHF **5** demonstrates the mechanochemical origin of the higher-intensity transient light emission in the presence of **3**.

Whilst being sensitive to mechanical force, the system is thermally very stable. At room temperature, no change was observed in the ^{1}H NMR spectrum of **2** in the presence of **3** over the course of a month, and no light could be observed from coumaranone **2** when a toluene solution with small molecule complex **4** was heated at 100 °C in toluene.

The chemiluminescence of adamantyl phenol dioxetane **1** was also readily induced by mechanically liberated NHC from **3**. When **1** (0.25 mm) was sonicated in a 1:1 mixture of toluene and acetonitrile with a polymeric palladium complex with a molecular weight of 50 kDa **3c** (0.25 mm), we observed significant light emission, which was clearly observable by eye in a darkened room and easily imaged with a consumer-level camera (Figure 3, inset). In this case, oxygen is not required for chemiluminescence from **1**, so the sonication could be run under methane, which is known to minimize the production of sonochemical impurities that deactivate the mechanically produced NHCs.[35] As a result of the high chemiluminescence intensity, we were able to inspect the spectroscopic details of the mechanoluminescent emitter. The emission spectrum of the mechanoluminescence under the conditions described above was found to be very similar to the emission spectrum obtained by inducing the chemiluminescence of **1** with a non-mechanical base, 1,8-diazabicycloundec-7-ene (DBU), as shown in Figure 3. This observation strongly suggests that the chemiluminescent decomposition of **1** is responsible for the observed mechanoluminescence.

As with coumaranone **2**, we also examined the time dependence of the mechanoluminescence emission from adamantyl phenol dioxetane **1** (Figure 4). The time–intensity trace obtained from **1** has similar features to those from **2**, but with higher intensity and a somewhat longer rise time, in part caused by the lower scission rate of the polymer complex under methane than under air ($3.2\times10^{-4}\,s^{-1}$ under methane and $1\times10^{-3}\,s^{-1}$ under air). The higher intensity reflects the higher quantum yield of **1**. To understand the time dependence of the luminescence in detail, we turned to kinetic modeling. Two-parameter fitting to a model consisting of essential elementary reaction steps (see the Supporting Information) indicated that the deprotonated phenol, stabilized by hydrogen-bonding to the imidazolium,[36–39] accumulates in the first 30 minutes as the mechanobase is slowly released into the system. Whilst the rate of formation of the reactive intermediate is greatest at the start of the sonication, the long lifetime of the dioxetane intermediate delays the peak in light emission significantly. Lastly, Figure 4 shows a sharp drop in light intensity when sonication ceases. We attribute this to the lifetime of the intermediate dioxetane lengthening as the temperature of the solution rapidly declines once sonication has stopped, from 25 °C to 2 °C over 20–30 seconds (the temperature of the solution returns to that of the coolant; see the Supporting Information). It can also be seen from Figure 4 that the light intensity does not drop to zero and decays much more slowly after ceasing sonication, which is consistent with a reduction in the decomposition rate constant for the mechanically generated intermediate dioxetane following sonication.

As for coumaranone **2**, **1** was found to be stable to the conditions of sonication by ^{1}H NMR spectroscopy. Sonicating a solution of **1** in 1:1 acetonitrile/toluene under methane did not produce detectable light emission. Sonicating a toluene solution of **1**, small molecule palladium complex **4** and unfunctionalized pTHF under methane gave out no detectable light, confirming the mechanical origin of the luminescence with the polymeric palladium complex.

In conclusion, we have demonstrated that mechanically generated base effectively induces chemiluminescence from two substrates, with polymeric palladium carbene complexes acting as a latent source of base. The time–intensity traces obtained were found to be consistent with the kinetics of the mechanobase production and chemiluminescent decomposition. Control experiments with the small molecule palladium complex and the dependence of the peak intensity on the molecular weight of the mechanobase substantiates the mechanical origin of the light emission. We envisage that this system or its future variants will be useful not simply as a means of generating light mechanically, but to probe bond scission processes with much greater sensitivity. Currently we are pursuing the development of complexes with greater mechanical lability and a system by which chemiluminescence is generated not stoichiometrically, but catalytically.

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