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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.
Metal NHC complexes are well known as thermally latent catalysts and bases. Our group has reported on the use of silver(I) and ruthenium(II) bis-NHC complexes centrally incorporated in poly(tetrahydrofuran) (pTHF) as mechanically latent catalysts for transesterification and metathesis reactions. The study at hand makes use of newly developed palladium bis-NHC complexes, which exhibit greater thermal stability than the silver complexes. 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 x 10^{-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 x 10^{-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 ~ 13 kDa (Figure S4, SI).

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) 3e (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 chemiluminescence 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 SI). The higher scission rates compete better against recoordination of the NHC to palladium, providing a greater initial “burst” in the concentration of free carbene.

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 solutions of coumaranone 2 alone were sonicated in the presence of air. We attribute this low
initiated by (non-mechanical) 1,8-ly liberated NHC from scission of placed beneath the flask. toluene at 25 °C. Light emission recorded with a photodiode curve) 1 adamantyl phenol dioxetane diazabicycloundec-7-ene (DBU, 50 mM) (red). Both spectra camera in combination with a spectrograph. Each spectrum represents the average of twenty sequentially recorded spectra. Spectra corrected for wavelength-dependent sensitivity of the detection complexes chemical activation of 0.2 mM solutions of palladium–NHC complexes none was heated at 100 °C in toluene.

thermally very stable. At room temperature, no change was observed in the 1H NMR spectrum of 2 when a toluene solution with small molecule complex 4 was sonicated for 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 3. Emission spectra of mechanoluminescence from adamantyl phenol dioxetane 1 (0.25 mM) initiated by mechanically liberated NHC from 3c (0.25 mM) (black) and of chemiluminescence of 1 initiated by (non-mechanical) 1,8-diazabicycloundec-7-ene (DBU, 50 mM) (red). Both spectra recorded in 1:1 toluene:acetonitrile, with an intensified CCD camera in combination with a spectograph. Each spectrum represents the average of twenty sequentially recorded spectra. Spectra corrected for 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 v/v at 25 °C. Upward arrows and downward arrows indicate the start and end of sonication respectively. The fit to the kinetic model (see SI) is shown by the red curve. The inset shows the control experiments with 1 alone (blue curve) or in the presence of 4 and 5 (green curve), also in methane-saturated toluene:acetonitrile 1:1 v/v at 25 °C. Light emission recorded with a photodiode placed beneath the flask.

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 x 10^-4 s^-1 under methane and 1 x 10^-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
tuned to kinetic modeling. Two-parameter fitting to a model consisting of essential elementary reaction steps (see SI) indicated that the deprotonated phenol, stabilized by hydrogen-bonding to the imidazolium, 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 SI). 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, I was found to be stable to the conditions of sonication by 1H NMR. Sonication a solution of I in 1:1 acetonitrile/toluene under methane did not produce detectable light emission. Sonication a toluene solution of 1, small molecule palladium complex 4 and unfunctionalised 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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NOTES

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