



Catalytic reduction of polar substrates without metals: A thermodynamic and kinetic study of heterolytic activation of hydrogen by vacancies in frustrated Lewis pairs



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ABSTRACT

Time-resolved reaction calorimetry provides a measure of the turnover frequency (TOF), ca. 1.1 min^{-1} , and enthalpic driving force, ca. -73 kJ/mol , for the metal-free catalytic reduction of an organic imine, *tert*-butylbenzalimine, (tBu-IM) with a frustrated Lewis acid–base pair, [2-(dimesitylphosphino)ethyl] bis(pentafluorophenyl)borane (PBCat), at 298 K and 13.8 bar hydrogen (H_2) pressure. Lowering the H_2 pressure by a factor of two decreases the TOF (0.6 min^{-1}), which is consistent with a pseudo first-order reaction in H_2 . In the absence of imine, the heat flux measured in the calorimeter provides a measure of the enthalpy for heterolytic splitting of H_2 , $\text{PBCat} + \text{H}_2 \rightarrow \text{PBCatH}_2$, ΔH ca. $-43(4) \text{ kJ/mol}$. Solution phase ^{19}F nuclear magnetic resonance spectroscopy was used to determine the rate of heterolytic splitting of H_2 by PBCat, $k = 0.7(3) \text{ M}^{-1} \text{ s}^{-1}$ and the equilibrium constant for $\text{PBCat} + \text{H}_{2(\text{soln})} \rightleftharpoons \text{PBCatH}_2$, $K_{\text{eq}}(295) = 2.2(5) \times 10^5 \text{ M}$, providing an estimate of the free energy for heterolytic splitting of H_2 , ΔG ca. $-29.8(1.3) \text{ kJ/mol}$ at 295 K in toluene. Deconvolution of the instrument time constant from the heat flux using the Tian equation shows the concentration of imine decreases linearly in time (i.e., the substrate imine is not involved in the rate limiting step, suggesting that H_2 activation by the Lewis acid–base pair is rate limiting).

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1. Introduction

A key objective in catalysis research is to advance the understanding of chemical transformations involved in catalytic reactions, thus enabling rational design of new, more energy efficient approaches in catalytic processes. Experimental methods that provide measurements of absolute rates, turnover frequencies (TOF), and reaction energetics provide critical insight into quantitative structure–reactivity relationships that set the energy landscapes defining catalytic processes. Insight into the physical and chemical properties that control the thermodynamics is just as important as insight into kinetics to avoid the formation of intermediates in a catalytic cycle that may be too stable and slow the overall process. Calorimetry has been a useful tool for studying catalytic transformations in liquid phase reactions [1]. Reaction calorimetry measures the time-dependent heat flow, Q , generated by the heat released from the reaction. The time-dependence of the heat flow

is directly related to the rate of the reaction, $\partial C/\partial t$, while the amplitude of the heat flux is related to the reaction enthalpy, ΔH_r , and reaction volume, V , as shown in Eq. (1).

$$Q = \partial C/\partial t * \Delta H_r * V \quad (1)$$

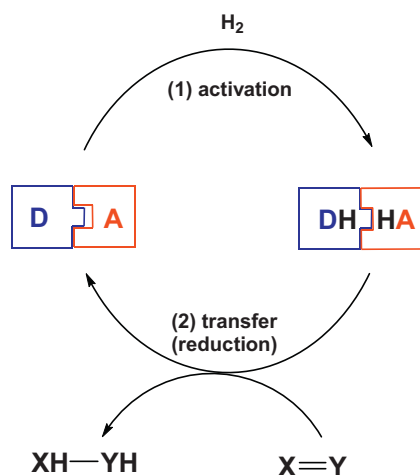
Reaction calorimetry has the advantage of being a differential measurement in which the heat flux provides a direct measure of the rate of reaction. The observable parameter is the rate, and the processed parameter is conversion (i.e., the change in concentration as a function of time). Hansen and co-workers have provided analytical solutions for obtaining kinetic rate data for a well behaved reaction (i.e., a reactant proceeding directly to a product) [2]. For reactions that occur on time scales comparable to the calorimeter's instrument time constant, τ , use of the Tian Eq. (2) provides an approach to deconvolute τ from the observed rate of change, Q_C , to obtain the experimental quantity of interest, Q_R , which is the rate of change in the signal due to the reactions of interest.

$$Q_R = Q_C + \tau(\partial Q_C/\partial t) \quad (2)$$

A focus of our research is to optimize the catalytic reduction of polar substrates at low temperatures to maximize energy efficiency

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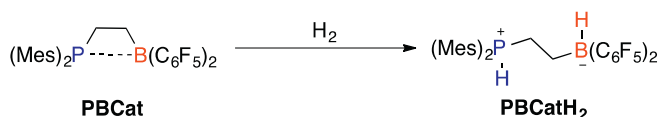
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Scheme 1. General scheme for FLP catalysis: Step 1, H₂ activation; Step 2, H₂ transfer.

of molecular transformations. Approaches that take advantage of multiple or dual catalytic reaction sites are of current interest. For example, combining both an acidic and a basic functionality into a single material or molecular framework has the potential to provide novel catalytic properties that are not observed by either the acid or base functionality individually [3,4]. One area in which acid–base cooperativity has received a great deal of recent attention in molecular catalysis is the metal-free catalytic reduction of polar substrates (e.g., imines and olefins) using frustrated Lewis acid–base pairs (FLP) [Scheme 1](#) [5,6]. A number of research groups have shown that designing steric constraints into a molecular complex to prevent or minimize quenching of Lewis acid/Lewis base pairs can result in unique reactivity not observed by the Lewis acid or Lewis base individually [7].

Although the concept of reversible H₂ activation by a non-metal FLP complex was only recently appreciated [8], there have been several researchers who have recognized the potential of these non-metal molecular complexes to act as catalysts that facilitate the heterolytic scission and transfer of H₂ to a number of polar and polarizable substrates [9–13]. One FLP catalyst in particular, 2-[(dimesitylphosphino)ethyl]bis(pentafluorophenyl)borane (PBCat), ([Scheme 2](#)) first developed by Erker and his coworkers, has been demonstrated to reduce a variety of substrates catalytically under mild conditions [14–18]. However, experimental efforts have produced little quantitative data on the kinetics and thermodynamics of the individual steps in the catalytic cycle [19]. In the study of H₂ activation and catalysis by FLPs, theory has been ahead of experimental evidence in providing insight into the novel reactivity. Papai and coworkers have used density functional theory (DFT) and continuum modeling of solvation to calculate the thermodynamic driving force for H₂ activation by a large number of FLPs [20]. The calculated $\Delta G(\text{calc})$ for heterolytic splitting of H₂ by PBCat in toluene is ca. -10 kJ/mol, which provides an estimate of the $K_{\text{eq}}(298\text{ K})=50$ for the equilibrium of $\text{PBCat} + \text{H}_2 \rightleftharpoons \text{PBCatH}_2$. The computational results are consistent with the experimental observation that this reaction proceeds rapidly and quantitatively to PBCatH₂ under moderate H₂ pressure. Theory has provided key insight into the nature of the transition state leading to H₂



Scheme 2. Heterolytic activation of H₂ by PBCat.

activation [20–29]. There appears to be little attractive interaction between the Lewis acidic borane and molecular H₂ in contrast to the dihydrogen complexes formed between unsaturated metal centers and molecular hydrogen [30–33]; however, the activation barrier for H₂ activation by PBCat is only 90 kJ/mol, calculated at the SCS-MP2/CBS level of theory [31].

In the results described below, we combine reaction calorimetry with nuclear magnetic resonance (NMR) spectroscopy to provide a measure of the TOF for the reduction of a polar imine substrate catalyzed by PBCat. We also measure the enthalpic driving force for H₂ activation by the FLP PBCat and H₂ transfer to an imine from PBCatH₂. The development of these kinetic and thermodynamic tools will be beneficial in providing not only the first relevant rate data to eventually benchmark one catalyst against another, but also thermodynamic data to benchmark computational predictions of the driving force for the heterolytic activation and transfer of hydrogen.

2. Experimental

2.1. Materials and methods

All manipulations were carried out under an inert nitrogen (N₂) atmosphere using standard Schlenk or glovebox techniques unless otherwise stated. Toluene was passed through a neutral alumina column under argon prior to use. *tris*(pentafluorophenyl)borane (BCF) was obtained from Boulder Scientific and purified by sublimation under reduced pressure at 90 °C. Bromobenzene was purified by distillation over CaH₂ prior to use. PBCat and PBCatH₂ were synthesized according to the available literature method [14]. All NMR spectra were recorded on 500 MHz Varian INOVA spectrometers. ¹⁹F NMR spectra were referenced using fluorobenzene as an internal standard ($\delta = -113.15$ ppm). Calorimetric measurements were performed on a Calvet calorimeter purchased from Setaram, C80. The instrument was operated in isothermal mode. Measurements were conducted in a modified Hastealloy® reversal mixing cell. The commercial mixing vessels were modified to include an inlet with 1/16 inch outer diameter PEEK tubing that allowed gases to be introduced. The instrument response was determined by measuring the heat of dissolving potassium chloride in aqueous media, thus providing an additional test of the instrument calibration relative to the accepted literature value for $\Delta H_{\text{diss}}(\text{KCl}/\text{H}_2\text{O})$. The return of $Q(t)$ to baseline takes ca. 280 s for this reaction assumed to be instantaneous. In our experiments, the integrated heat flow, $Q(t)$, was collected at 1.5-s intervals until the heat signal returned to baseline, thus providing thousands of data points to be used in processing the reaction conversion.

2.2. Calorimetry experiments

Reaction calorimetry was performed in a Setaram Calvet calorimeter fitted with mixing cells modified to perform variable pressure experiments. The first set of experiments provided a measure of the heat released in the exothermic reaction of PBCat with H₂ to form the zwitterionic PBCatH₂ in bromobenzene or toluene solutions (2 mL, 0.025 M) and 12.6 bars of H₂ pressure. A second set of experiments provided a measure of the heat released in the stoichiometric reduction of *tert*-butylbenzalimine (1.0 mL, 0.076 M) by the zwitterionic PBCatH₂ (1.0 mL, 0.10 M) under 1 atmosphere of N₂. A third set of experiments provided a measure of the heat released under catalytic reaction conditions, PBCatH₂ (1 mL, 0.022 M) and imine (1 mL, 0.51 M) at two pressures, 5.8 and 13.9 bars of H₂. In a typical experiment, the catalyst PBCatH₂ and substrate imine were placed in separate chambers of a *sample* cell (see supplemental Fig. 1S) and the solvent, bromobenzene

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