Catalysed low temperature H_2 release from nitrogen heterocycles

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In an experimental and computational study, nitrogen- and oxygen-containing heterocycles were compared with carbocycles as liquid substrates for hydrogen release with heterogeneous catalysts. Heteroatom substitution, particularly by nitrogen, favours low temperature H_2 release; indoline was fully dehydrogenated in less than 30 min with Pd/C at 110 °C.

Hydrogen has been suggested as a possible energy carrier for future automotive applications.[1] Assuming the problem of H_2 generation can be adequately addressed, hydrogen storage and transport pose a major challenge. To date, no single material fulfils all the criteria ideally required for a satisfactory hydrogen storage material, which must absorb and release with rapid kinetics and operate at moderate temperatures (60–120 °C). It must also be inexpensive and have high gravimetric and volumetric capacities. Liquefaction of hydrogen consumes a large amount of energy and needs extensive thermal insulation, whereas compressed gas requires heavy containment tanks[2] and poses a release hazard. Hydrogen absorption in solid hydrides is a better alternative but air and water instability is a serious limitation.[1] Carbon nanotubes, decorated,[3] or not,[4] with metallic nanoparticles, are a promising possibility.

Organic liquids have been much less studied, largely because typical catalytic hydrogen release reactions, such as cyclohexane to benzene, are strongly endothermic and so require prohibitively high release temperatures. Several homogeneous[5–9] and heterogeneous[10,11] catalysts are efficient in catalytic alkane dehydrogenation. For instance, Saito and co-workers showed the activity of Wilkinson's catalyst at 180 °C for the conversion of cyclooctane to cyclooctene[5] and carbon- and alumina-supported catalysts for the slow conversion of cyclohexane to benzene.[10]

Production of H_2 from formic acid is much easier but the formation of CO_2 is a drawback.[12,13] Alcohols can be readily dehydrogenated in the presence of catalysts such as ruthenium complexes.[14,15] Very recently, Thorn and co-workers[16a] have reported that benzimidazolines can release H_2 readily, and related work is in progress.[16b]

In this paper, we show how the inclusion of one or more heteroatoms, such as O and especially N, into the model organic structures can favour H_2 release, both thermodynamically and kinetically, thus lowering the H_2 release temperatures into a more practically useful range. In particular, thermodynamic calculations and experiments with heterogeneous catalysts show that dehydrogenation is possible even at modest temperatures (110 °C). Structure–activity trends in our model substrates should help identify better candidates for future studies. We only look at the release step in this paper because arene hydrogenation is much better documented; for hydrogen storage applications, H_2 release has to be easy because it would be carried out in the vehicle itself.

Results and discussion

Dehydrogenation reactions of typical hydrocarbons such as cyclohexane are substantially endothermic but our calculations show that the presence of one or more nitrogen atoms lowers the unfavourable enthalpy of the reaction. Calculations were performed at the DFT level using the 6-31++G** basis set (Fig. 1).

The isolobal replacement in cyclohexane/benzene of one CH_2/CH fragment by NH/N causes a reduction of 5.78 kcal mol^{-1} in the endothermicity. The replacement by a second NH/N has different consequences depending on its position: *ortho* is unfavourable, while *para* and especially *meta* lead to further reductions of 3.74 and 5.27 kcal mol^{-1}, respectively. Thermodynamically, triazinane is the easiest to dehydrogenate, the reaction being endothermic by only 13.72 kcal mol^{-1}. We ascribe the beneficial effect on the thermodynamics to the well known weakening effect of adjacent nitrogen on a CH bond. The BDE of the ethane CH bond[17] is 98 kcal mol^{-1} but that of methylamine CH bonds is only 90 kcal mol^{-1}.[18] Additionally, NH bonds tend to be slightly weaker than analogous CH or OH bonds.[17]

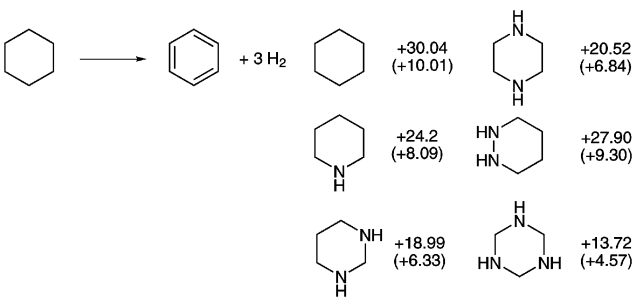

Fig. 1 Enthalpy of dehydrogenation of several N-containing heterocycles. In brackets: average value per H_2 molecule released (kcal mol^{-1}).

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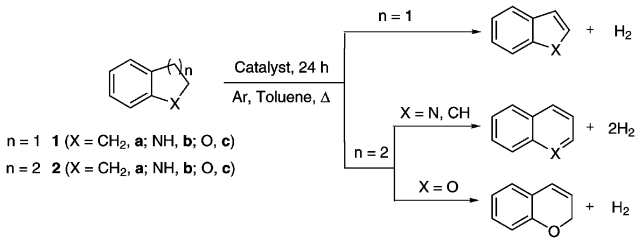

Fig. 2 Potential dehydrogenation of **1a–c** and **2a–c**.

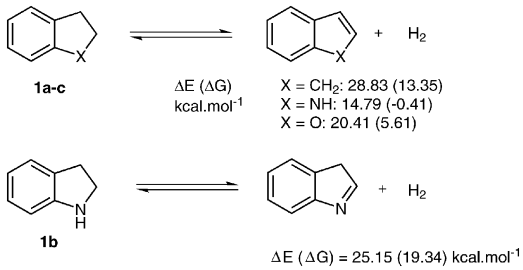

Fig. 3 Computed thermodynamic values (kcal mol^{-1}) for the dehydrogenation of bicyclic compounds **1a–c**.

Several readily available model compounds were tested experimentally to study their ease of dehydrogenation. Bicyclic compounds containing an aromatic ring fused with a saturated five- or six-membered heterocycle were first tested. Analogous oxygen, nitrogen and carbon derivatives could thus be directly compared (Fig. 2).

In our procedure, substrates were heated under reflux of toluene for 24 hours in the presence of the catalyst (1 mol% based on metal). The reaction mixture was degassed and heated under a stream of argon, both to avoid the presence of air and to enable the venting of any dihydrogen formed. This procedure drives the H_2 release, as previously shown in the related problem of alkane dehydrogenation,[5,6] under so called acceptorless conditions (*i.e.* in the absence of a sacrificial alkene as oxidant). Heterogeneous catalysts known for dehydrogenation reactions were chosen for study: Pd/C, Rh/C and Rh/Al_2O_3. The results, presented in Table 1, show the strong promoter effect of N as the heteroatom: indoline (**1b**) was the most promising model substrate. Both Pd/C and Rh/C fully converted it into its dehydrogenation product, indole, after 24 hours in refluxing toluene. Even after only 30 min, complete conversion was obtained with Pd/C. Rh/Al_2O_3 was less active, with a 43% conversion in 24 hours. Control reactions show that in the absence of catalyst or with the supports alone (*i.e.* C or Al_2O_3) we see no conversion under comparable circumstances. This point is crucial as the organic liquids chosen should, for safety reasons, be stable upon heating in the absence of catalyst. In the series of six-membered heterocycles, only the bicyclic compound 1,2,3,4-tetrahydroquinoline (**2b**) gave the fully dehydrogenated compound (quinoline), the aromatic stabilisation of which clearly drives the double dehydrogenation.

For completeness, some experiments were also carried out with **1b** in the presence of air, where O_2 now becomes the oxidant. Interestingly, Rh/Al_2O_3 was now found to be the most active (99% conversion in 24 hours) compared to Pd/C (95%) and Rh/C (41%) all under the same conditions.

In order to confirm the evolution of hydrogen, the gas generated from the reaction of indoline (**1b**) in the presence of Pd/C (1 mol%) was passed through a second solution containing *cis*-cyclooctene and Pd/C (1 mol%). The latter reaction mixture was stirred at room temperature for 7 hours, and the generation of cyclooctane was observed and confirmed by ^1H NMR spectroscopy and GC-MS, thus confirming the presence of H_2 in the gas stream.

A computational study was undertaken to rationalise the experimental observations. Thermodynamic values for dehydrogenation reactions of the bicyclic compounds **1a–c** and **2a–c** were calculated at the DFT/B3LYP level using the 6-311+G(d,p) basis set (Fig. 3, 4 and 5). All the calculated reactions are endothermic, but variations are observed depending on the ring size (5 or 6) and the nature of the heteroatom X. In the five-membered ring series (**1a–c**, Fig. 3), the formation of indole from **1b** is strongly favoured (14.79 kcal mol^{-1}) over the formation of indene from **1a** (28.83 kcal mol^{-1}) or benzofuran from **1c** (20.41 kcal mol^{-1}). Indole is also more stable, by 10.36 kcal mol^{-1}, than its imine isomer. The latter point and the ease of indoline (**1b**) dehydrogenation over indane (**1a**) dehydrogenation can be ascribed to the nitrogen atom α to the double bond stabilising the molecule by aromatic delocalisation.

The computational study rationalises the experimental results (Table 1) as the only five-membered substrate that could be easily dehydrogenated at low temperatures by catalysis is indoline (**1b**). In the case of the six-membered ring series (Fig. 4 and 5), dehydrogenation involves the formation of several potential isomers and, if X = C or N, double dehydrogenation also has to be considered. The mono-dehydrogenations of **2a–c**, with reaction enthalpies lying between 27 and 32 kcal mol^{-1}, are more complicated, whatever isomers are formed,

Table 1 Dehydrogenation reactions (% conversion) of heterocyclic substrates **1a–c** and **2a–c** with heterogeneous catalysts

Substrate	Pd/C^a	Rh/C^a	$Rh/Al_2O_3{}^a$	C^b	Al_2O_3
1a (X = CH_2)	0%	0%	0%	0%	0%
2a (X = CH_2)	13%	0%	0%	0%	0%
1b (X = NH)	100%	100%	43%	0%	0%
2b (X = NH)	50%	24%	4%	0%	0%
1c (X = O)	0%	0%	0%	0%	0%
2c (X = O)	0%	0%	0%	0%	0%

[a] Metal/support = 5 wt%. [b] Activated charcoal.

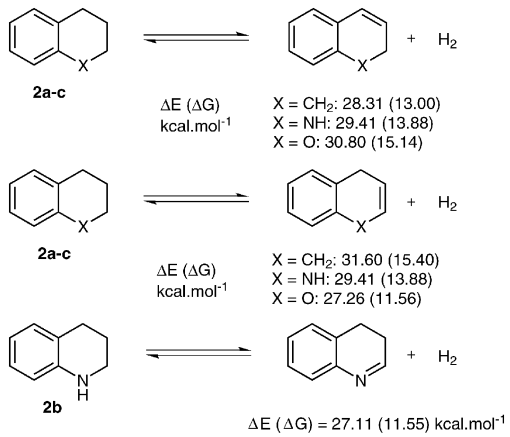

Fig. 4 Computed thermodynamic values (kcal mol^{-1}) for the mono-dehydrogenation of bicyclic compounds **2a–c**.

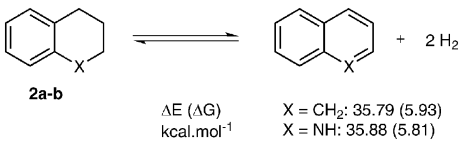

Fig. 5 Computed thermodynamic values (kcal mol^{-1}) for the double dehydrogenation of bicyclic compounds **2a–b**.

compared to those of **1a–c**. When double dehydrogenation is considered, the enthalpies shift to 35.79 for X = CH_2 and 35.88 kcal mol^{-1} for X = NH. These numbers are not much higher than those obtained for mono-dehydrogenation because the molecules formed are aromatic. Indeed, the calculated aromatic stabilisation has been estimated to be *ca.* 30 kcal mol^{-1}.[19,20] But ΔE values per H_2 molecule released (17.90 and 17.94 kcal mol^{-1} for X = CH_2 and NH, respectively) are useful for comparison. In fact, the experimental results show that **2a** and **2b** can indeed be dehydrogenated under our conditions and that complete selectivity towards the aromatic, fully dehydrogenated compounds is observed. No reaction was observed with **2c** (X = O) because full dehydrogenation is impossible and the enthalpy of mono-dehydrogenation is very high.

Conclusions

Experimental and computational work shows that nitrogen atoms strongly promote the dehydrogenation of organic liquids, with H_2 evolution, both thermodynamically and kinetically, permitting reaction even at 110 °C.

Experimental

Materials

Indane **1a**, 1,2,3,4-tetrahydronaphthalene **2a**, indoline **1b**, 1,2,3,4-tetrahydroquinoline **2b**, dihydrobenzofuran **1c**, palladium on carbon (5%) and rhodium on carbon (5%) were purchased from Aldrich and used as received. Rhodium on alumina (5%) was purchased from Matheson Coleman and Bell. Dry and degassed toluene was purchased from Alfa Aesar. Chroman (**2c**) was obtained according to the literature.[21,22] Catalytic yields were determined by ^{1}H NMR spectroscopy.

Dehydrogenation procedure

1 mmol of the substrate was placed in 5 mL of dry and degassed toluene in the presence of 1 mol% of the catalyst (based on the metal). The solution was refluxed under an argon stream for 24 hours before analysis.

Computational methods

All calculations were carried out at density functional theory (DFT) level using Becke's three-parameter hybrid functional[23] and the Lee–Yang–Parr correlation functional[24] (B3LYP) as implemented in GAUSSIAN 03.[25] The 6-31++G** basis set was employed for all elements in the calculations presented in Fig. 1. For the rest of the theoretical study, the 6-311+G(d,p) basis set was used for C, N and O atoms and the 6-31G basis set for H atoms.[26–28] The stationary points located at the DFT/B3LYP level were characterised by frequency calculations. Frequency calculations have been performed to include the zero-point energy correction.

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