Computational structure–activity relationships in H_2 storage: how placement of N atoms affects release temperatures in organic liquid storage materials

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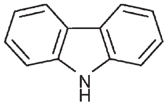
DFT(B3PW91) calculations show that release of H_2 is greatly favored thermodynamically in five membered rings over six and by the incorporation of N atoms into the rings, either as ring atoms or as ring substituents, particularly in 1,3 positions.

Hydrogen has often been suggested as a potential energy carrier in automotive applications[1] but fully satisfactory H_2 storage methods are still lacking. Current methods do not approach the exceptionally high energy density, both volumetric and gravimetric, of conventional fuels such as hydrocarbons and alcohols if the container weight is also considered.

High pressure tanks and reversible storage in solid materials are well established,[2] but the attractive possibility of using an organic liquid as storage medium has not yet received sufficient attention in spite of its many advantages. Distribution would be possible with existing infrastructure, no high pressures are involved, and free H_2 is only produced as needed *via* a catalytic dehydrogenation step, both minimizing the risk of metallurgical degradation on contact with H_2 and avoiding high pressures. Such materials could also plausibly be made available in the required quantity (estimated to be *ca.* 10^{12} kg). In addition, improved gravimetric capacities are possible in this way. Methylcyclohexane/toluene has been studied, but the dehydrogenation is both kinetically and thermodynamically unfavorable, requiring both a highly active catalyst and elevated temperature.[3] Lower release temperatures are needed.

In the liquid H_2 carrier scheme, a generalized hydrogenated carrier, A_h, gives up hydrogen to form the fully dehydrogenated form A_d by a catalyzed thermal process. In an important prior patent by Pez and coworkers,[4] as well as in our own previous report,[5] it was shown both computationally and experimentally that incorporation of N or, less satisfactory, O into the heterocycle A_h facilitates dehydrogenation in part by decreasing the endothermicity of the reaction. Thorn and coworkers have reported that benzimidazolines can release H_2 readily.[6]

In their patent, Pez and coworkers use a variety of aza and polyaza heterocycles, notably carbazoles, for hydrogen storage and report DFT calculations on the thermodynamics of a much wider variety of A_h/A_d pairs. In our prior paper,[5] we reported indoline dehydrogenation with Pd/C at 100 °C and DFT calculations of the energy of reactions for a small range of azaheterocycles.


carbazole

Here we extend the computational work to a wider range of azaheterocycles to try to define general rules that govern the relationship between the heterocycle structure and the endothermicity of dehydrogenation. The heterocycles discussed here are chosen to reveal general trends and not as practical hydrogen storage materials, because numerous factors other than the thermodynamics, such as toxicity, volatility, liquid state, ease of access *etc.*, need to be considered. 'Real' A_h/A_d pairs would doubtless be involatile, for example.

Table 1 shows the list of A_d compounds studied and reports the thermodynamic data per H_2 released (ΔH_d, ΔG_d, ΔS_d; B3PW91/aug-cc-pVDZ calculations) for the A_h to A_d conversion, given both for one mole of A_h and A_d.† The *N*-methyl 5-membered ring species were also calculated to avoid artefacts associated with unstable N–H tautomers. The calculated enthalpies of reaction show that the dehydrogenation process is endothermic for all systems shown in Table 1. The calculated values for ΔH_d are in excellent agreement with the experimental values when available (see Table 1, linear regression correlation coefficient of 0.9985).

To gain an idea of the effect of a change of structure on the release temperature, we have used the data to calculate T_d, the temperature at which the calculated ΔG_d is zero. The ΔH_d and ΔS_d values were assumed to be independent of the temperature (Ellingham approximation) and T_d was thus estimated as $\Delta H_d/\Delta S_d$.[7] Experimental release temperatures will differ from T_d because each individual dehydrogenation stage has, in principle, its own equilibrium temperature. However trends in T_d values obtained with the above assumptions should nevertheless be valuable indicators in designing A_h/A_d pairs.

Table 1 shows the vast range of T_d achievable (molecules are listed in order of increasing T_d value), going from *ca.* 50 K to *ca.* 1000 K. This implies that judicious choice of heterocycle should allow T_d to be fixed at almost any desirable point in the range. Each practical application may well require different T_d values and if so a knowledge of the trends in T_d would be useful. T_d cannot be too high or dehydrogenation becomes difficult, nor too low because hydrogenation would be too hard. The second problem is less severe since hydrogenation would occur on an industrial scale in a central facility where high H_2 pressures and severe conditions could be used. The resulting fuel would then be distributed much

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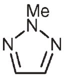
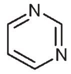
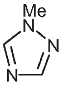
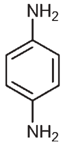
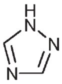
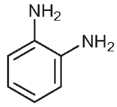
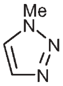
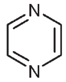
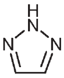
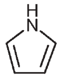
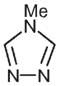
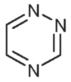
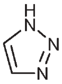
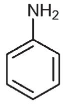
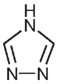
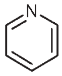
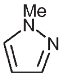
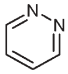
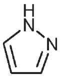
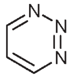
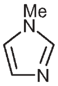
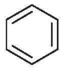
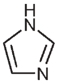
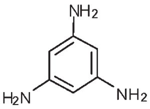
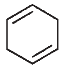
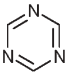
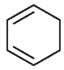
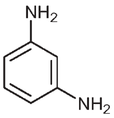
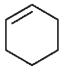
Table 1 Thermodynamic data (ΔH_d, ΔG_d, kcal mol^{-1}; ΔS_d, cal mol^{-1} K^{-1}) per H_2 molecule released as obtained from B3PW91/aug-cc-pVDZ calculations. T_d (K) is the temperature corresponding to $\Delta G_d = 0$. When available, experimental values for ΔH_d are given in parentheses. The fully dehydrogenated molecules are shown

A_d	ΔH_d	ΔG_d	ΔS_d	T_d		ΔH_d	ΔG_d	ΔS_d	T_d
	1.4	−7.7	30.6	46		14.3	5.5	29.6	483
	1.5	−7.3	29.8	50		14.6	5.7	29.8	490
	3.2	−5.4	28.8	111		15.0	6.0	30.	500
	3.4	−5.4	29.7	114		15.0(13.6)	6.2	29.6	507
	3.3	−5.2	28.4	116		14.8(13.4)	6.3	28.5	520
	4.7	−3.7	27.0	174		15.7	6.8	29.8	527
	5.3	−3.2	28.4	187		15.7(15.3)	6.9	29.5	532
	6.3	−2.3	28.9	218		16.1(14.9)	7.3	29.5	546
	7.1	−2.0	30.8	230		16.6	7.7	29.7	559
	8.3	0.0	27.8	298		16.9	8.0	29.7	569
	9.3	0.5	29.6	314		17.6(16.4)	8.9	29.4	599
	9.5	1.1	28.5	333		27.3(25.7)	18.8	28.7	951
	11.6	2.8	29.5	393		29.4(27.2)	20.3	30.6	961
	13.0	4.1	29.8	436		29.5(27.2)	20.5	30.1	980
	13.7	4.8	29.6	463		30.2(28.4)	21.1	30.5	990

as petrol (mogas) is today, but the A_d form recovered for hydrogenation, unlike current practice.

As expected the ΔS_d per H_2 released is essentially constant at +29 ± 1.5 kcal mol^{-1}, because this value is dominated by the variation in the molecularity of the reaction (release of H_2),[8] and not by differences in the entropy of A_h and A_d.

Lowering T_d requires that the unsaturated species be made more stable or that the saturated systems be less stable. Factors that may stabilize the unsaturated species are for instance the strength of the π bonds (the hydrogenation enthalpies of ethylene and methanimine are -32.6 and -21.2 kcal mol^{-1}, respectively)[9] and the aromatic character of the π systems. Factors that may influence the energy of the saturated species include the bond energies of the C–H and N–H bonds (N substituents are well known to weaken α-CH bonds, for example),[10] and the interactions between bonds and/or lone pairs.[11] These factors are expected to be involved in determining some of the trends noted in Table 1 but further work is needed for a better understanding of the detailed rationalization.

The largest structural influence on T_d is the difference between the 6-membered rings with high T_d and the 5-membered rings with lower values. This may simply be the result of achieving full aromaticity after breaking only four NH or CH bonds in the 5-membered A_h rings *versus* six such bonds in the 6-membered cases. Consistent with this picture, cyclopentadiene is an exception, having a very high T_d, presumably because it is not aromatic.

Why is the Pez–Cooper carbazole[4] so effective? The single N atom can be considered as a ring atom in the 5-membered B ring and as a substituent atom for each of the 6-membered rings A and C. We therefore consider ring N and substituent N effects.

Comparison of benzene (T_d = 599 K), pyridine (T_d = 546 K) and aniline (T_d = 532 K) suggests that a substituent N can be even more effective than a ring N in lowering T_d. For larger effects we need additivity, however, and this indeed appears to hold when the N atoms are in a 1,3-arrangement. Comparison of benzene (599 K), aniline (532 K), 1,3-diaminobenzene (463 K) and 1,3,5-triaminobenzene (393 K) shows that the effects are approximately additive for substituent N. The same additivity also approximately holds for ring N atoms in a 1,3-arrangement: benzene (599 K), pyridine (546 K), 1,3-diazine (483 K) and 1,3,5-triazine (436 K).

In contrast, a 1,2-arrangement of ring N atoms is not desirable as shown by 1,3-diazine (483 K) *versus* 1,2-diazine (559 K). This is presumably a manifestation of the alpha effect, where two adjacent N lone pairs in an arene suffer mutual repulsion and destabilize A_d.[10] A 1,4-placement is also somewhat unfavorable as shown by 1,4-diazine (507 K). Positional effects in N-substituents behave somewhat similarly as shown by the series 1,2-diaminobenzene (500 K), 1,3-diaminobenzene (463 K), and 1,4-diaminobenzene (490 K), but the mechanism is different: the two adjacent NH_2 groups in the 1,2-isomer clash sterically and are twisted so as to decrease the N lone pair to arene conjugation. Additivity applies as shown by 1,3,5-triaminobenzene (391 K).

In summary, this work points to a number of design factors that can be applied to tune the T_d value in any desired direction over a vast range. Five-membered rings tend to be most effective in lowering T_d. Both ring and substituent N atoms are effective and with 1,3-placement, additivity applies.

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Notes and references

† DFT calculations have been performed with the Gaussian03 package[12] at the B3PW91 level[13] with Dunning's aug-cc-pVDZ basis sets.[14] The molecules were optimized without any symmetry constraint and the nature of the extrema located (minima) was checked through analytical calculations of the frequencies. The latter calculations were used to compute the thermodynamic properties (H, G, S and c_v) as provided by G03. For the hydrogenated products, all the possible conformations of the 5- or 6-membered rings were searched for and the most stable one was used to compute the thermodynamic properties.

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7 The influence of the temperature on the ΔH_d and ΔS_d values was estimated using calculated c_v values according to $\Delta H_d(T) = \Delta H_d(298) + (\Delta c_v/n + R)*(T - 298)$ and $\Delta S_d(T) = \Delta S_d(298) + (\Delta c_v/n + R)*\ln(T/298)$, assuming A_h and A_d are in the same physical state and n is the number of H_2 molecules released. The equation $\Delta G_d = 0$ was solved for T and the T_d values obtained did not differ significantly (*ca.* -5 to -15 K) from the ones reported in Table 1, except for the last four items where deviations up to -70 K were obtained.

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