Hydrogenolysis without hydrogen gas: hydrogen loaded palladium electrodes by electrolysis of $H[NTf_2]$ in a room temperature ionic liquid

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Electrochemical hydrogenolysis has been demonstrated in a room temperature ionic liquid (RTIL) for the first time. Reduction of $H[NTf_2]$ at a Pd microelectrode in the RTIL 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_2mim][NTf_2]$) leads to the reversible formation of adsorbed and absorbed hydrogen (Pd/H). Hydrogenation of *N*,*N*′-bis(benzyloxycarbonyl)-L-lysine was observed to proceed rapidly, monitored by the consumption of Pd/H. In addition, the electrolysis of adventitious H_2O to form Pd/H is noted.

Introduction

Hydrogenation and hydrogenolysis reactions have extensive and diverse applications, and catalytic hydrogenation reactions have been extensively investigated and reviewed in room temperature ionic liquids (RTILs).[1,2] Typically such reactions involve the use of H_2 gas in pressurised vessels in conjunction with a suitable catalyst. Alternatively, transfer-hydrogenation involves the introduction of an additional species that decomposes to produce hydrogen on contact with the catalyst.

Electrochemical hydrogenation or hydrogenolysis offers a means of *in situ* hydrogen generation (such as *via* the electrochemical reduction of a labile proton) thus bypassing both the use of large quantities of potentially explosive H_2 gas, and the generation of a stoichiometric equivalent of waste commonly found in transfer-hydrogenation reactions. Surprisingly, to the best of our knowledge such electrochemical techniques have not been previously demonstrated in an RTIL.

RTILs are of extensive interest to electrochemists, as all RTILs possess inherent conductivity, and other properties such as high thermal and chemical stability, extremely low vapour pressure, high solubility and tuneable physical properties are widely available.[3] Due to these characteristics they can, in principle, be extensively recycled without producing atmospheric pollution.

Certain RTILs can also dissolve extensive quantities of a wide variety of biomass materials, which makes them promising solvents for the processing of these renewable materials.[4] Hydrogenolysis of cellulose[5] and biomass derivatives[6] in RTILs using H_2 gas and Ru catalysts has recently been reported. The electrochemical hydrogenolysis of biomass compounds[7] is one possible green, clean and safe route to convert these macromolecular compounds into useful chemical feedstocks.

As proof-of-concept, the hydrogenolysis of *N*,*N*′-bis(benzyloxycarbonyl)-L-lysine was investigated. By employing a Pd microelectrode the experiments were carried out under well defined conditions, and also correspond to the first investigation of such reactions at a microelectrode. A labile proton was reduced at the Pd electrode and hydrogenolysis of *N*,*N*′-bis(benzyloxycarbonyl)-L-lysine proceeded rapidly at room temperature, displaying proof-of-concept that RTILs can be used for such processes.

Results and discussion

Initially, the electrochemistry of a Pd microelectrode was investigated in the presence of a labile proton source in the IL $[C_2mim][NTf_2]$. Fig. 1 displays a scan rate study for scans recorded in the presence of 100 mM $H[NTf_2]$ in $[C_2mim][NTf_2]$. With the introduction of $H[NTf_2]$ a reduction wave is clearly observed, corresponding to the reduction of H^+ and concurrent absorption/adsorption of H onto and into the Pd matrix. On the reverse sweep the oxidation of the absorbed/adsorbed H is observed with release of H^+ back into solution. The electrochemistry of $H[NTf_2]$ has previously been investigated in $[C_nmim][NTf_2]$ RTILs at Pt, Au and GC electrodes,[8,9] and a diffusion coefficient of 3.2×10^{-11} m^2 s^{-1} was determined for $H[NTf_2]$ in $[C_2mim][NTf_2]$.[9] The limiting current displayed in Fig. 1 corresponds to *ca.* 50% of that expected for the known *D* value. This is partially due to the nature of the reduction process, where kinetic limitations can also apply due to the gradual saturation of the palladium lattice, as demonstrated in Fig. 1 by the broadness of the reduction wave after the sweep is reversed at *ca.* −1.1 V. Partial volatilisation (*in vacuo*) of the $H[NTf_2]$ prior to the experiment is also a possibility, although CVs recorded

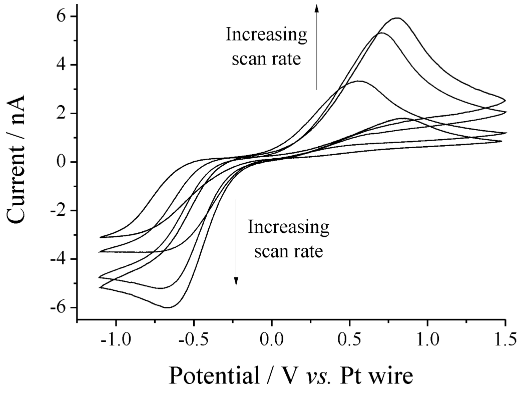

Fig. 1 Scan rate study (10, 50, 100, 500 and 1000 mV s^{-1}) for the reduction and oxidation of 100 mM $H[NTf_2]$ at a 4.7 μm radius Pd microelectrode in $[C_2mim][NTf_2]$, *in vacuo*.

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as a function of time demonstrated that this contribution was minimal (< 10%) within the first 8 h.

The removal of *O*- and *N*-benzyl protection groups is frequently performed using Pd/C and H_2 gas.[10] Due to the low solubility of H_2 this process often takes a number of hours to go to completion. Mandal and McMurray[11] have reported the transfer-hydrogenation of a wide variety of compounds by the addition of triethylsilane to Pd/C, resulting in the *in situ* generation of molecular hydrogen. This included the rapid quantitative or near quantitative hydrogenolysis of benzyloxycarbonyl-protected ((*Z*)-protected) species in 10–50 min. It should be noted that while this method bypasses the use of H_2, triethylsilane is water-sensitive, highly flammable, has a flashpoint of –4 °C, and generates a stoichiometric equivalent of waste.†

Reduction of the H[NTf_2] at the Pd microelectrode will result in the formation of reactive Pd/H. If hydrogenolysis occurs on the timescale of the CV, hydrogen will be consumed from the Pd/H resulting in a corresponding decrease in the size of the oxidation peak on the reverse scan. Fig. 2 displays scans recorded for 200 mM H[NTf_2] in the presence of various concentrations of *N*,*N*′-bis(benzyloxycarbonyl)-L-lysine (*Z*-lys(*Z*)-OH). Solutions of H[NTf_2] and *Z*-lys(*Z*)-OH were tested over a number of days and no change in voltammetry was observed, demonstrating no prior decomposition of the starting material. Slight shifts in the position of each peak are related to slight changes in the quasi-reference potential. As the concentration of *Z*-lys(*Z*)-OH is increased the limiting current for proton reduction decreased. This is due to the two amine groups present in *Z*-lys(*Z*)-OH, which become protonated in the presence of H[NTf_2] and thus decrease the available concentration of protons. In addition the oxidation peak on the reverse scan also decreases, though it decreases in size relatively more rapidly than that of the proton reduction wave.

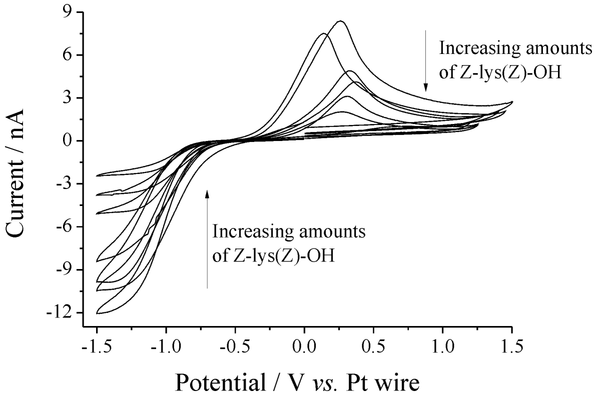


Fig. 2 Scans recorded for various concentrations of *Z*-lys(*Z*)-OH (0 to 80 mM) in the presence of 200 mM H[NTf_2] in [C_2mim][NTf_2] at a 4.7 µm Pd microelectrode, at 100 mV s^{-1} and *in vacuo*.

The relative changes in the two peaks were quantified by integration of both processes, followed by dividing the oxidation charge by the reduction charge in order to obtain the corresponding ratio. Fig. 3 plots the change in the ratio with the concentration of *Z*-lys(*Z*)-OH, demonstrating that as the concentration of *Z*-lys(*Z*)-OH increases, progressively less Pd/H remains on the reverse scan. This is attributed to the relatively rapid hydrogenolysis of the *Z*-lys(*Z*)-OH, Scheme 1 displays the expected hydrogenolysis reaction. However, the Pd/H is not completely consumed on the time scale of the scan as the proton is expected to diffuse relatively more rapidly than the bulky *Z*-lys(*Z*)-OH molecule, resulting in relatively more H[NTf_2] reaching the electrode than *Z*-lys(*Z*)-OH. Fig. 4 plots a scan rate study for 200 mM H[NTf_2] and 40 mM *Z*-lys(*Z*)-OH. The inset plots the change in ratio in the oxidation and reduction charge, and clearly demonstrates that as the scan rate increases relatively less Pd/H is consumed, as would be expected.

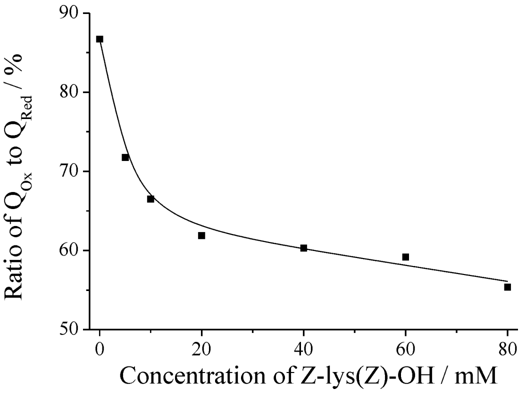
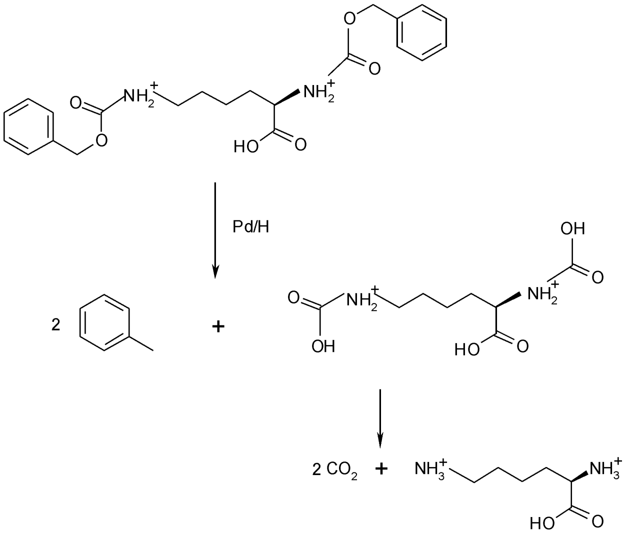


Fig. 3 Plot of the ratio of oxidation charge to reduction charge (corresponding to formation and removal of Pd/H) for various concentrations of *Z*-lys(*Z*)-OH (0 to 80 mM) for the CVs shown in Fig. 2.



Scheme 1 Reaction scheme of the hydrogenolysis of *Z*-lys(*Z*)-OH with Pd/H.

By performing this hydrogenolysis at a microelectrode, the electrochemical processes and chemical reaction occur in a well-defined system, and subsequent simulation of these results could yield fundamental parameters regarding the chemical reaction occurring at the Pd/H-RTIL interface.

It should be noted that the experiments were carried out *in vacuo*. This was necessary as H_2O-contamination of RTILs is rapid, and results in a dramatic reduction of the electrochemical window due to the facile electrolysis of the H_2O.[12] The electrolysis of trace H_2O in RTILs has been demonstrated to proceed smoothly with the production of H_2 and O_2 at the cathode and anode, respectively.[13] In this work it was noted that the dissolved H_2O omnipresent in RTIL samples before vacuum

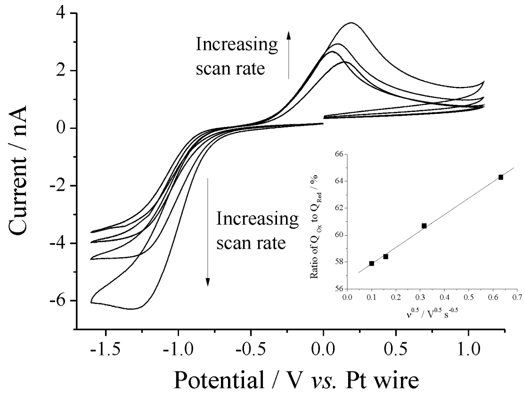


Fig. 4 Scan rate study (10, 25, 100 and 400 mV s^{-1}) for 40 mM *Z*-lys(*Z*)-OH and 200 mM H[NTf_2] in [C_2mim][NTf_2] at a 4.7 μm Pd microelectrode. The inset plots the ratio of oxidation charge to reduction charge *vs.* the square root of scan rate.

drying could be readily reduced to form Pd/H. Such a system could potentially be employed for green hydrogenation and hydrogenolysis reactions, with H_2O as the hydrogen source, RTIL as the recyclable electrolyte (with unique solvation capabilities) and O_2 as the only by-product.

Conclusions

By demonstrating the rapid hydrogenolysis, proof-of-concept has been achieved indicating that room temperature ionic liquids can be used for electrochemical hydrogenolysis. Hydrogenolysis of *N*,*N*′-bis(benzyloxycarbonyl)-L-lysine was achieved by the electrochemical reduction of a labile proton at a Pd microelectrode, and the hydrogenolysis monitored by the size of the Pd/H oxidation peak. The extension of this system to hydrogenation reactions should present no great problems.

Experimental

The RTIL 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [C_2mim][NTf_2] (ultra-pure grade) was kindly donated by Merck KgaA. *N*,*N*′-Bis(benzyloxycarbonyl)-L-lysine (>98.0%) was purchased from Sigma Aldrich and used as received. Electrochemical experiments were performed using a computer-controlled μ-Autolab potentiostat (Eco-Chimie, Netherlands). A conventional three-electrode arrangement was employed, with a Pd electrode (4.7 μm radius) as the working electrode, and two Pt wires as quasi-reference and counter, respectively. The tip of a disposable micropipette was used as a neck for the clean working electrode, into which 20 μL of RTIL could be accommodated. Electrochemistry was performed *in vacuo* in a glass T-cell designed for investigating μL-scale samples of RTIL under a controlled atmosphere.[3] The RTIL solutions were purged under high vacuum for *ca.* 180 min, to remove trace atmospheric moisture and gases naturally present in the ionic liquid.

Notes and references

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