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LETTER

DDQ as an electrocatalyst for amine dehydrogenation, a model system for virtual hydrogen storage†

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2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) is an electrochemical oxidation catalyst for a secondary amine, a model system for virtual hydrogen storage by removal of a hydrogen equivalent from an amine; a computational study provides mechanistic information.

Electrodehydrogenation reactions are sought for use in fuel cell applications.^{1–3} In this context, saturated N-containing heterocycles^{1,2} have been proposed as electrochemical (virtual hydrogen storage)¹ or thermal liquid carriers for $2(\text{H}^+ + \text{e}^-)$ or for H_2 , respectively. Pez² *et al.* have shown how a fuel, *N*-ethyl carbazole, can be both hydrogenated and dehydrogenated catalytically over many cycles with a heterogeneous catalyst. The presence of N in the molecule makes the less favorable reaction, dehydrogenation, more thermodynamically and kinetically favorable.¹ A ubiquitous feature of the proposed systems is the CH–NH motif. To this date no molecular catalyst is able to perform the desired dehydrogenative oxidative transformation under electrochemical conditions. As a proof of principle, we use *N*-phenylbenzylamine (**Ia**) to illustrate an organocatalytic CH–NH group dehydrogenation.

We explore quinones as dehydrogenation electrocatalysts, relying on their known ability to perform $2(\text{H}^+ + \text{e}^-)$ chemistry. In particular we find that the high potential quinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), dehydrogenates the *model* substrate PhCH_2NHPH (**Ia**) to give $\text{PhCH}=\text{NPh}$ (**Ib**). Known for aromatizing a wide variety of saturated heterocycles,⁴ we now find DDQ can abstract two H atom equivalents from the NH–CH₂ group, not only stoichiometrically but *via* electrochemical organocatalysis. DDQ is commonly used as a stoichiometric oxidant and it readily reacts with water,⁴ so aqueous solvents must be avoided. Several reports on its non-aqueous electrochemistry are available,^{5–7} although none in the context of dehydrogenative amine oxidations.

We now find that the stoichiometric oxidation of either *N*-phenylbenzylamine or indoline (**Ila**) with DDQ in benzene gives satisfactory yields (86% of **Ib**; 97% of **Ilb**) of unsaturated products after only 30 s at room temperature (see also ESI†). This rapid reaction avoids the slow H_2 evolution step in the Pez study.² Our computational analysis of the underlying reaction mechanism, at the DFT BH&H/6-311++G(d,p) level, indicates that *N*-phenylbenzylamine and DDQ form a tight 1 : 1 complex, stabilized by stacking and charge-transfer interactions (Fig. 1). Approximately 0.25 *e* units of charge are transferred from *N*-phenylbenzylamine to DDQ, giving zwitterionic character to the complex, and a strong electrostatic attraction that brings the stacked aromatic moieties in close contact with each other. The interaction of a carbonyl moiety of DDQ with a benzyl hydrogen of *N*-phenylbenzylamine leads to hydride transfer, forming the highly unstable intermediate (ion pair), with even stronger zwitterionic character. Rotation of the deprotonated hydroquinone, stacked to the benzylamine ring in the ion pair, is almost barrierless and leads to deprotonation of the benzyl ion forming hydroquinol and completing the dehydrogenation of *N*-phenylbenzylamine. The overall dehydrogenation reaction is exothermic, releasing $\sim 35 \text{ kcal mol}^{-1}$.

Catalysis requires electro-regeneration of an active quinol radical species. A prior study on anodic regeneration of DDQ from the corresponding hydroquinone reports the substoichiometric use of DDQ as an electrocatalyst for the side chain oxidation of 2-methyl and 2-benzyl naphthalenes with O_2 , suggesting the potential for broader electrocatalytic use of this oxidant.^{6,7} From a synthetic standpoint, imines are versatile intermediates in the synthesis of substituted amines.⁸ Electrochemistry is considered one of the cleanest ways to perform desired chemical transformations⁹ therefore the mediated electrooxidation of primary amines to the corresponding nitriles¹⁰ provides an important precedent in the dehydrogenation of C–N bonds. Moreover, only one electrochemical imine synthesis has previously been reported.¹¹

We find that catalytic DDQ mediated amine oxidation is possible (Fig. 2). Initial cyclic voltammetry indicated that electrolysis at 0.964 V vs. NHE (see ESI†) would allow DDQ regeneration from its hydroquinone (which forms immediately after addition of quinone to substrate). In a controlled

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† Electronic supplementary information (ESI) available: Experimental details include ¹H and ¹³C NMR chemical shifts of all products as well as electrochemical and computational data. See DOI: 10.1039/c0nj01011a

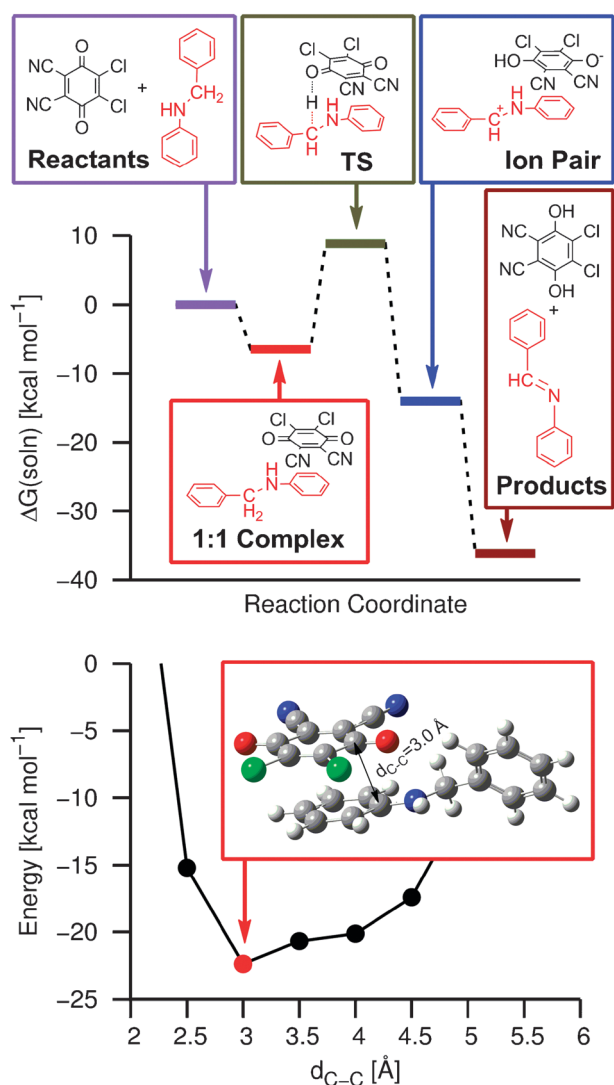


Fig. 1 (top) Free energy diagram for dehydrogenation of *N*-phenylbenzylamine in benzene solution by oxidation with DDQ, which occurs *via* formation of a 1 : 1 reactive complex (bottom) stabilized by stacking and intermolecular charge-transfer interactions, as described at the DFT BH&H/6-311++G(d,p) level of theory.

potential electrolysis in a two-chamber cell with 15% quinone loading (0.5 M NaClO₄, acetonitrile) we get 95% imine yield after 6 hours. To the best of our knowledge, this is the first case of DDQ being employed as a mediator in an electrocatalytic dehydrogenative process. Indoline is not a suitable substrate however because, although current passes, anodic deposition of organic material occurs and indole is not recovered. Electrolysis in the absence of quinone leads to polymeric decomposition products.

Conclusion

We have successfully performed secondary benzylic amine dehydrogenation in the presence of a metal-free organocatalyst. This proof of principle introduces high potential quinones as

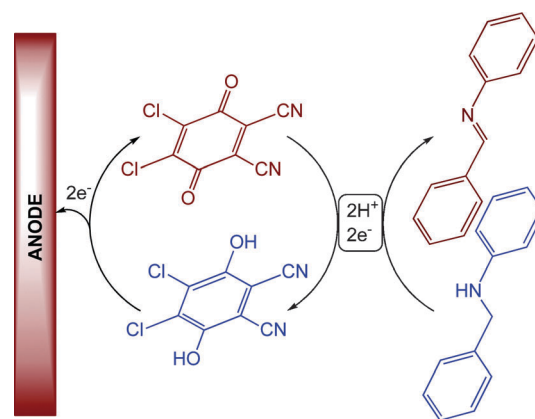


Fig. 2 Dehydrogenation of *N*-phenylbenzylamine by DDQ-mediated electrooxidation at a Pt anode *via* controlled potential electrolysis at 0.964 V vs. NHE¹² in acetonitrile/sodium perchlorate (0.5 M) at 21° under continuous Ar purge.

organic mediators in organic electrodehydrogenation processes. Further work is needed to optimize the method and expand the substrate scope of this transformation. Organocatalysis is proposed as an alternative to heterogeneous catalysis in such dehydrogenation processes.

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