Supporting Information for Electrochemical Oxidation of *N*-Nitrosodimethylamine with Boron-doped Diamond Film Electrodes

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6-Pages

5-Figures

1. Quantum Mechanics Simulations. Transition state searches were performed using a quadratic synchronous transit (QST) method (*1*) and refined using an eigenvector-following method (*2*). The energy optimized structures and transition states were verified by frequency calculations. Imaginary frequencies with wave numbers smaller than 10 cm^{-1} were considered numerical artifacts of the integration grid and convergence criteria (*3*).

2. Flow-through Reactor.

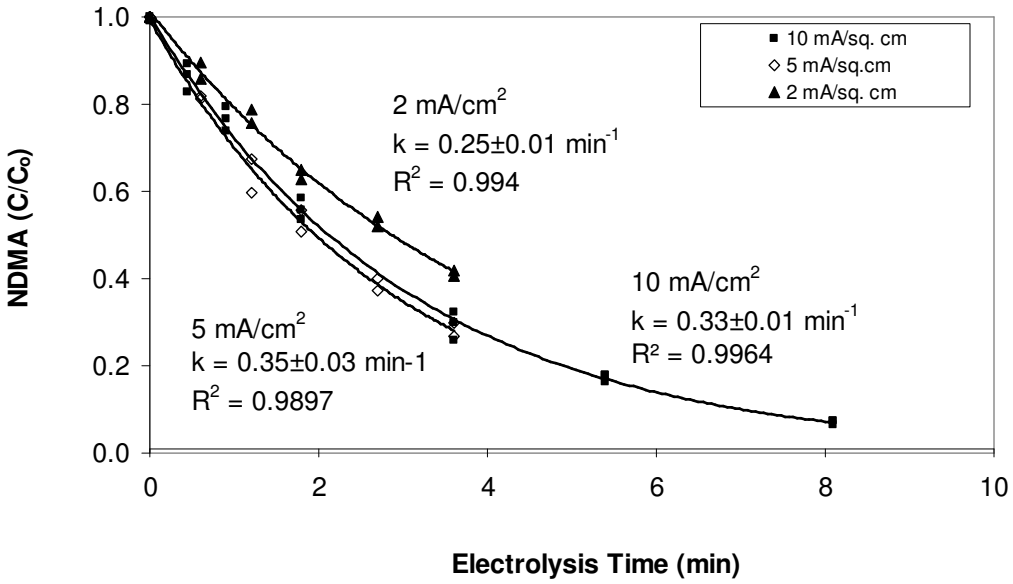

Figure S-1. Effect of current density on NDMA removal in the flow-through reactor. Solid lines represent regression of replicate experiments. Reported errors represent 95% confidence intervals.

3. Calculation of Activation Barrier for NDMA

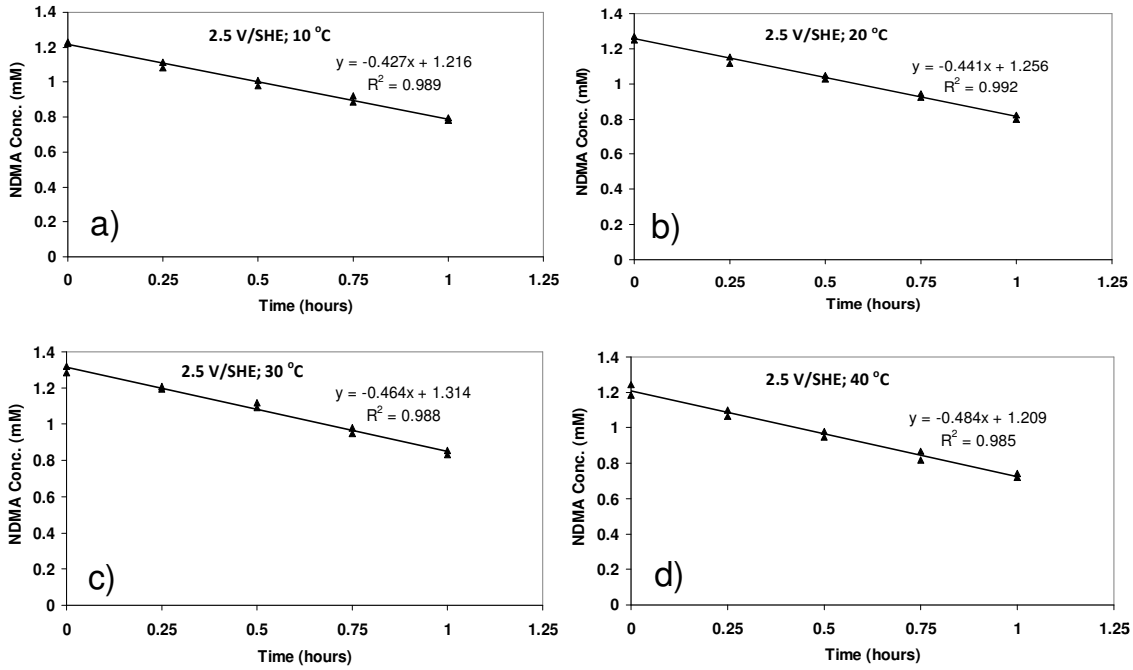

Figure S-2. Plot of NDMA oxidation during batch experiments at a constant potential of 2.5 V/SHE, in 50 mL of a 1 M $HClO_4$ background electrolyte using a 1 cm^2 BDD electrode, at temperatures of: a) 10 °C, b) 20 °C, c) 30 °C, and d) 40 °C. Solid lines represent linear regressions of duplicate experiments.

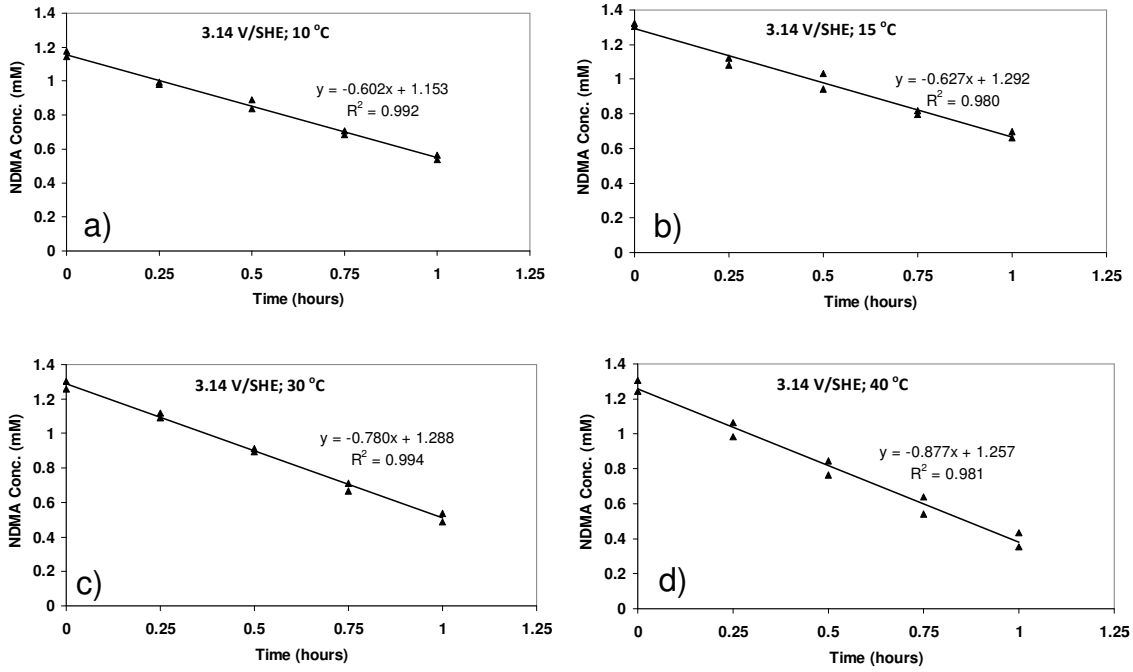

Figure S-3. Plot of NDMA oxidation during batch experiments at a constant potential of 3.14V/SHE, in 50 mL of a 1 M $HClO_4$ background electrolyte using a 1 cm^2 BDD electrode, at temperatures of: a) 10 ^oC, b) 15 ^oC, c) 30 ^oC, and d) 40 ^oC. Solid lines represent linear regressions of duplicate experiments.

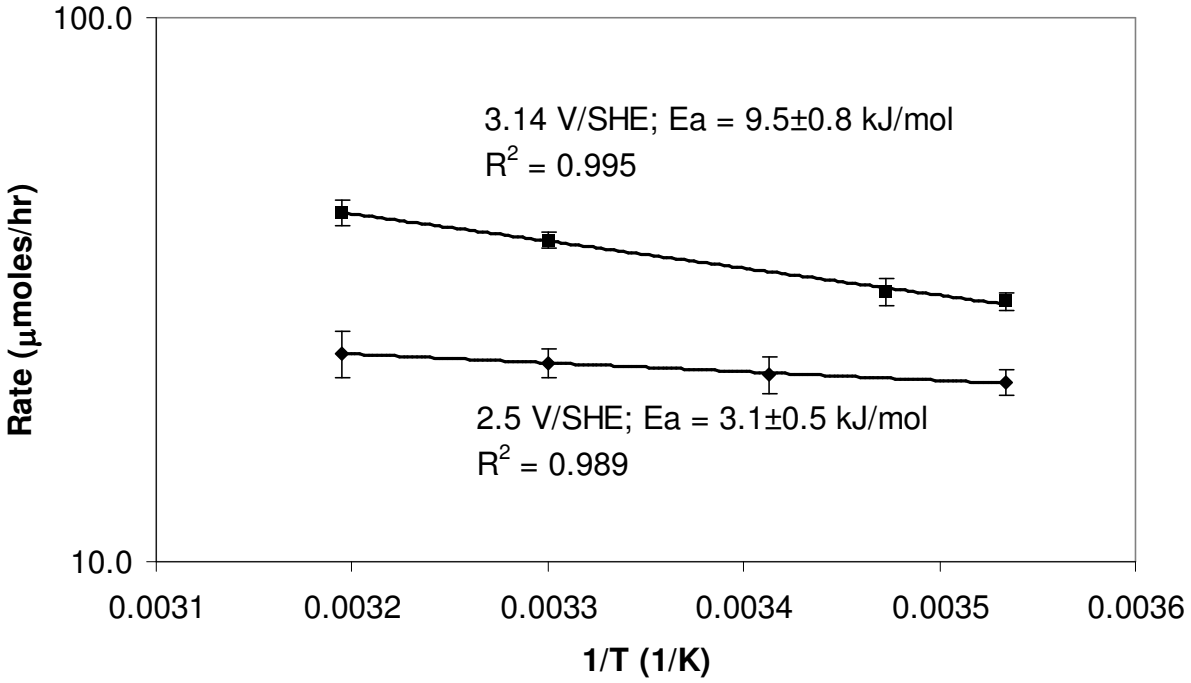

Figure S-4. Initial rates of NDMA oxidation versus reciprocal temperature at potentials of 2.5 and 3.14 V/SHE. Error bars represent 95% confidence intervals on rates. Confidence intervals (95%) are also shown for values determined for E_a. Solid lines represent regressions.

4. DFT Results. Structures from DFT calculations for NDMA, $NDMA^{(+1)}$, and $NDMA^{(+2)}/H_2O$ adduct are shown in Figure S-5 below. The water adduct stabilizes the $NDMA^{(+2)}$ molecule by 201 kJ, which is close to the average N-O bond strength of 230 kJ/mol. The loss of two electrons from NDMA results in shortening of the N=O and N-N bonds from 1.255 to 1.200 Å, and 1.321 to 1.261 Å, respectively. All other bond lengths remained approximately the same.

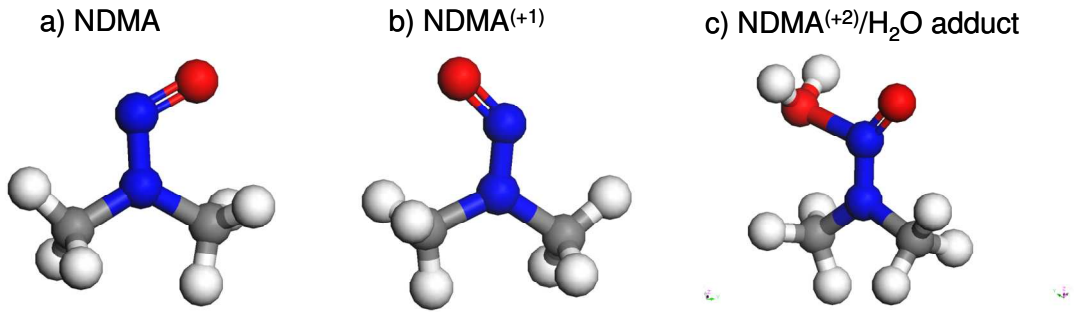

Figure S-5. Molecular structures for: a) NDMA, b) $NDMA^{(+1)}$, and c) $NDMA^{(+2)}/H_2O$ adduct. Atom key: C = gray; N = blue; O = red; H = white.

5. References

(1) Halgren, T. A.; Lipscomb, W. N., The synchronous-transit method for determining reaction pathways and locating molecular transition states. *Chem. Phys. Lett.* **1977,** *49*, 225-232.

(2) Fischer, S. K., M., Conjugate peak refinement: An algorithm for finding reaction paths and accurate transition states in systems with many degrees of freedom. *Chem. Phys. Lett.* **1992,** *194*, 252-261.

(3) Ochterski, J. W., Vibrational analysis in gaussian. Available at www.gaussian.com/vib.htm (accessed June 2008).