

Reduction of Nitrosobenzenes and *N*-Hydroxylanilines by Fe(II) Species: Elucidation of Reaction Mechanism

DALIZZA COLÓN,^{*,1} ERIC J. WEBER¹ JAMES L. ANDERSON,² PAUL WINGET,¹ AND LUIS A. SUÁREZ¹

U.S. Environmental Protection Agency, National Exposure Research Laboratory,
960 College Station Road, Athens, Georgia 30605-2720¹
Department of Chemistry, University of Georgia, Athens, Georgia 30602-2556²

Environmental Science & Technology

SUPPORTING INFORMATION

04/12/2006

8 Pages
3 Tables

Experimental Section

Chemicals. Nanopure water (Barnstead) was boiled under argon for 20 min, followed by continued purging with argon for four additional h. Degassed water was used throughout this work to prepare all aqueous solutions and oxide suspensions. The oxygen level in purged water was measured by the Indigo Carmine method (using Accu Vac Ampules from Hach Co.); the oxygen level was not different from zero.

The *p*-substituted HAs, with the exception of *N*-hydroxylaniline, were prepared by the addition of zinc and ammonium chloride to a stirred solution of the corresponding *p*-substituted nitrobenzene in acetone (1). The products were treated as follows. CNHA was extracted with ether and crystallized twice from ether to give yellow crystals. AcHA was extracted with ethyl acetate and fractionated on silica gel. Crystallization from ether/ethyl acetate/hexane gave pale yellow crystals. ClHA was extracted with ether and crystallized from ether/hexane to get pale yellow shiny plates. BrHA was extracted with ether and crystallized from ether/hexane to get pale yellow shiny crystals. MeHA was extracted from the aqueous solution with ether and crystallized from ether/hexane to give colorless leaflets. HHA was synthesized by the reduction of nitrobenzene with zinc in ammonium chloride in water as reported by Kamm and Marvel (2). The product was crystallized from ether/hexane to give colorless needles. All purified products were stored in the dark under inert gas.

CNNO was made by oxidation of *p*-aminobenzonitrile, dissolved in dioxane, with persulfuric acid (H_2SO_5) as reported by Ashley and Berg (3). The product, a yellow solid, was purified by steam distillation and crystallization from methanol. MeNO was prepared by reduction of *p*-nitrotoluene, dissolved in acetone, to *p*-methyl-*N*-hydroxylamine with zinc and ammonium chloride followed by oxidation with ferric chloride as reported by Fletcher, et al. (1). The

product was purified by steam distillation and crystallization from methanol to give a colorless solid.

Minerals. Goethite (α -FeOOH) was synthesized by pumping slowly (≈ 30 mL/min) 2.2 L of 0.26 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 0.1 N HNO_3 into 5.0 L of 0.73 M KOH solution in a water bath at 10 °C. After mixing, the precipitate was aged at 70 °C for 24 h (4,5). Hematite (α - Fe_2O_3) was obtained by adding 16.6 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to 2 L of 0.002 M HNO_3 that had been heated to 98 °C in a flask in an oven. The mixture was stirred vigorously and the flask was closed and returned to the oven immediately and kept at 98 °C for seven days (Schwertman, 1991 #272). Lepidocrocite (γ -FeOOH) was synthesized by dissolving 11.93 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in 300 mL water with stirring. The pH was adjusted to 6.4 to 6.8 with 1 N sodium hydroxide. The reaction mixture was purged with a flow of air of 280 mL/min. The reaction was completed when the desired pH range was attained (Schwertman, 1991 #90). Between each successive synthesis batch, the pH probe was cleaned with 0.1 N HCl and 0.1 M EDTA as described in pH probe maintenance procedures. 2-Line Ferrihydrite (Fe_5HO_8) was prepared by the addition of 160 mL of a 0.5 M KOH solution into 1 L of 0.1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution in the absence of air with stirring. The pH of the final mixture was 7.24.

Once the syntheses were finished, the supernatants of the mineral suspensions were decanted followed by freezing and freeze-drying of the minerals at -70 °C and 8 μm Hg. The identities of goethite, hematite and lepidocrocite were verified by X-ray powder diffraction analysis. The surface area of the various oxides was determined by the BET method (6) using a Micromeritics ASAP2000 (Micromeritics Inc.) surface area analyzer.

Analysis of Organic Compounds. Separation and detection of the analytes in 100 μL -sample aliquots were achieved using a Hewlett Packard 1050 reversed-phase HPLC equipped with an

autosampler, a quaternary pump and a diode array detector (UV-VIS). An Alltech Adsorbosphere C-18 guard cartridge (7.5 x 4.6 mm, 5 μ m) was used in combination with a 150 x 4.6 mm Waters Symmetry C18 analytical column (5 μ m). Mixtures of acetonitrile (J. T. Baker) and a degassed 20-mM phosphate buffer (made up of K_2HPO_4 and KH_2PO_4 from J. T. Baker at pH 6.6), in ratios anywhere from 16:84 to 40:60, were used in an isocratic mode at a flow rate of 1.0 mL/min to resolve all species of interest. The detection wavelength was set to the absorption maximum λ_{max} (nm) of the compound of interest at the condition of analysis (i.e., 273 for CNHA, 301 for AcHA, 242 for ClHA, 243 for BrHA, 232 for HHA, 234 for MeHA, 273 for CNAN, 313 for AcAN, 277 for ClAN, 243 for BrAN, 235 for HAN, 234 for MeAN, 285 for CNNO, 306 for HNO and 319 for MeNO).

Fe(II) Analysis. HCl (TraceMetal Grade, Fisher) was used to make Fe(II) stock solutions and prepare samples for Fe(II) analysis. Ferrozine [3-(2-Pyridyl)-5,6-bis(4-phenylsulfonic acid)-1,2,4-triazine monosodium salt monohydrate, Fluka] was used to measure Fe(II) as in Strathmann and Stone (7,8). Stock solutions of Fe(II) were prepared by adding 0.15 mL of 1 M HCl to 1.5 mL of 0.02 μ m-filtered (Anotop) 1.1 M $FeCl_2$ solution. Surface-associated Fe(II) was assessed as the difference between $Fe(II)_{aq}$ before and after the addition of a ferric oxide in suspension.

Results and Discussion

TABLE S1. Kinetic Data and Molecular Descriptors for *p*-Substituted *N*-Hydroxylanilines

<i>p</i> -substituent	k_{HAS} (h ⁻¹) ^a	SD ^b	p <i>K</i> _a ^c	σ _p ^d	EA (eV) ^e	E _{LUMO} (eV) ^f	BDE (kJ/mol) ^g
Me	0.902	0.089 (4)	-0.30	-0.170	-0.935	0.00290	177.0
H	0.543	0.034 (3)	-0.70	0	-1.11	0.00120	181.2
Br	0.510	0.046 (3)	-1.46	0.23	-0.756	-0.0135	183.1
Cl	0.507	0.015 (3)	-1.43	0.23	-0.721	-0.0138	182.4
Ac	0.116	0.012 (3)	-2.17	0.50	0.271	-0.0442	191.3
CN	0.0897	0.0024 (2)	-3.35	0.66	0.307	-0.0401	191.9

^aAverage pseudo-first order rate constant calculated from the linear regression of the concentration data (Ln [HA]/[HA]₀) versus time (h). ^bCalculated standard deviation (95%) of k_{HAS} and number of replicate experiments. ^cCalculated ionization constants by SPARC (9).

^dHammett σ constants (10). ^eCalculated electron affinities by SPARC (11). ^fCalculated lowest-occupied molecular orbital energies in the aqueous solution using B3LYP/6-31G*, SM5.42R.

^gCalculated bond dissociation enthalpy in the aqueous solution using B3LYP/6-31G*, SM5.42R.

TABLE S2. Effect of Oxide Surface Area Loading on the Rate of Reduction of *p*-Cyano-*N*-Hydroxylaniline

Surface Area Loading (m ² /L)	k_{CNHA} (h ⁻¹) ^a	$\pm\text{CL}$ (1/h) ^b
	Goethite	
1.03	1.96E-03	2.05E-03
5.61	2.93E-02	3.4E-03
11.2	1.01E-01	1.2E-02
28.1	2.02E-01	7.4E-02
56.1	3.94E-01	3.5E-02
84.2	5.65E-01	2.77E-01
112	5.93E-01	4.07E-02
	Lepidocrocite	
0.990	2.41E-04	3.70E-04
5.87	1.34E-02	4.60E-03
11.7	2.76E-02	1.0E-03
29.4	5.68E-02	6.7E-03
58.7	9.29E-02	9.4E-03
88.1	1.08E-01	1.1E-02
117	1.18E-01	1.06E-01
	Hematite	
0.552	7.51E-04	1.68E-03
0.829	2.17E-03	4.14E-03
1.11	3.11E-03	6.0E-04
6.02	4.39E-02	4.5E-03
12.0	9.02E-02	4.0E-04
30.1	1.77E-01	2.4E-02
60.2	3.25E-01	3.66E-01

^aAverage pseudo-first order rate constant calculated from the linear regression of the concentration data ($\ln [\text{CNHA}]/[\text{CNHA}]_0$) versus time (h) for duplicate experiments.

^bCalculated confidence limits (95%) for $k_{\text{CNHA}} = \pm\text{CL}$, where $\text{CL} = ts/N^{1/2}$. N = number of replicate experiments, $t = 12.7$ and s is the standard deviation.

TABLE S3. Effect of pH on the Rate of Reduction of *p*-Cyano-*N*-hydroxylaniline in Fe(II)-treated Hematite Suspensions^a

pH	k_{CNHA} (h ⁻¹) ^b	$\pm\text{CI}^c$
7.67	2.43E-02	4.96E-05
7.50	2.28E-02	2.73E-03
7.28	1.49E-02	2.75E-04
7.00	9.74E-03	4.78E-04
6.80	5.67E-03	3.27E-05
6.60	3.11E-03	6.70E-05
6.10	9.86E-04	1.49E-05

^aConditions: 15 μM CNNB, 1.3 m²/L hematite, 375 μM Fe(II), 25 mM of sulfonic acid buffer and 0.1 M NaCl. ^bAverage pseudo-first order rate constant calculated from the linear regression of the concentration data ($\text{Ln} [\text{CNHA}]/[\text{CNHA}]_0$) versus time (h) for duplicate experiments.

^cCalculated confidence limits (95%) for $k_{\text{CNHA}} = \pm\text{CL}$, where $\text{CL} = ts/N^{1/2}$. N = number of replicate experiments, $t = 12.7$ and s is the standard deviation.

Literature Cited

- (1) Fletcher, D. A. Structural investigations of C-nitrosobenzenes. Part 1. Solution state ^1H NMR studies. *J. Chem. Soc. Perk. Trans.* **1997**, 2, 2201-2206.
- (2) Kamm, O.; Marvel, C. S. β -Phenylhydroxylamine. *Org. Syn. Coll.* **1941**, 1, 445-447.
- (3) Ashley, J. N.; Berg, S. S. The search for chemotherapeutic amidines. 14. Congeners 4-4'-Diamidinoazobenzene. *J. Chem. Soc. Perk. Trans.* **1957**, 3089-3093.
- (4) Atkinson, R. J.; Posner, A. M.; Quirk, J. P. Adsorption of potential-determining ions at the ferric oxide-aqueous electrolyte interface. *J. Phys. Chem.* **1967**, 71, 550-558.
- (5) Torrents, A.; Stone, A. T. Hydrolysis of phenyl picolinate at the mineral/water interface. *Environ. Sci. Technol.* **1991**, 25, 143-149.
- (6) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of gases in multimolecular layer. *J. Am. Chem. Soc.* **1938**, 60, 309-319.
- (7) Strathmann, T. J.; Stone, A. T. Reduction of the carbamate pesticides oxamyl and methomyl by dissolved Fe^{II} and Cu^{I} . *Environ. Sci. Technol.* **2001**, 35, 2461-2469.
- (8) Colón, D.; Weber, E. J.; Anderson, J. L. QSAR study of the reduction of nitrobenzenes by Fe(II) species. *submitted to Environ. Sci. Technol.*
- (9) Hilal, S. H.; Karickhoff, S. W.; Carreira, L. A. A rigorous test for SPARC's chemical reactivity models: Estimation of more than 4300 ionization pK_{a} s. *Quant. Struct.-Act. Relat.* **1995**, 14, 348-355.
- (10) Hansch, C.; Leo, A. *Exploring QSAR. Fundamentals and Applications in Chemistry and Biology.*; ACS: Washington, DC, 1995.
- (11) Hilal, S. H.; Carreira, L. A.; Karickhoff, S. W.; Melton, C. M. Estimation of electron affinity based on structure activity relationship. *Quant. Struct.-Act. Relat.* **1993**, 12, 389-396.