

A LONG-LIVED IMINOXYL RADICAL BY ELECTROOXIDATION OF 1-NITROSO-2-NAPHTHOL*

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Cyclic voltammetry of 1-nitroso-2-naphthol in the potential region 0 to 1.0 V vs Ag/AgCl using glassy carbon and platinum electrodes shows a reversible redox couple. The electrode process is diffusion controlled and corresponds to an EC mechanism. The one-electron oxidation product, an iminoxyl radical, is characterized by a triplet ESR signal at $g = 2.0067$ further split by three ring hydrogens. This radical is unusually long-lived, with half-life times of 150 s in water and 3600 s in acetonitrile.

INTRODUCTION

Searching for stable radicals and compounds with potential application as spin traps, we turned our attention to 1-nitroso-2-naphthol (NN). Nitroso compounds are known to give stable spin adducts and are commonly used as spin traps.¹ Electrochemical radical generation from aromatic nitroso spin traps was investigated by Cauquis *et al.*² and later by Gronchi and Tordo.³ In the presence of certain oxidizing agents or under photochemical conditions, NN itself can be converted into radical species. Thus oxidation of NN to iminoxyl radicals with silver(II) complexes was reported by Jezierski.⁴ In a series of papers, Lagercrantz and co-workers⁵ reported the formation of radicals, from 1-nitroso-2-hydroxy compounds, including NN, by ammonium hexanitratocerate(IV) and under photochemical conditions.

Whereas cathodic reduction of *o*-nitrosophenols has been investigated by polarography,⁶ no voltammetric study of NN oxidation has been reported. In this paper, we report studies of NN in aqueous and acetonitrile media by cyclic voltammetry (CV) using solid electrodes and characterization of the anodic oxidation product by ESR spectroscopy. Results of *ab initio* calculations are presented and used to support the proposed mechanism.

EXPERIMENTAL

1-Nitroso-2-naphthol (Fisher) was recrystallized from ligroin (b.p. 60–90 °C) (m.p. 109 °C). Solvents were of reagent or chromatography grade and chemicals used for preparation of buffers were reagent grade. Aqueous solutions were prepared with distilled water. Most measurements were performed in 0.2 M HClO₄, 0.2 M NaHCO₃, and 0.01 M NaOH aqueous solutions. Other buffer solutions were prepared by combining the following solutions:⁷ pH 1.50 (0.2 M HCl + 0.2 M KCl), pH 3.50 (0.1 M potassium phthalate + 0.1 M HCl), pH 6.00 (0.1 M NaH₂PO₄ + 0.1 M NaOH), pH 8.00 (0.1 M TRIS + 0.1 M HCl), pH 10.00 (0.025 M borax + 0.1 M NaOH) and pH 12.00 (0.05 M Na₂HPO₄ + 0.1 M NaOH).

Instrumentation. A PC-interfaced Eco-Tribo polarograph (PolaroSensors, Prague, Czech Republic) with ETP software for storing and processing data was used in CV. The cell was equipped with a glassy carbon or Pt working electrode and an Ag/AgCl reference electrode (all from BAS) for aqueous solutions and for non-aqueous solutions with a laboratory-prepared Ag/Ag⁺ electrode in acetonitrile and a platinum wire auxiliary electrode. ESR–electrochemical experiments utilized an ESC 410 potentiostatic controller, a Varian E-4 spectro-

* Presented in part at the 29th Middle Atlantic Regional ACS Meeting, Washington, DC, May 24–26, 1995.

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meter and a 0.3 mm thick ESR cell (Wilmad 813). The latter was furnished with a flattened Pt wire working electrode in the flat part and a reference and auxiliary electrodes in the stem part (Figure 1). A M 270 EG&G potentiostat was used for chronocoulometric measurements, in a thin-layer cell (BAS) with a 0.1 mm spacer and a built-in glassy carbon electrode with data recorded on a PC. An IBM EC 219 rotating disk electrode with a glassy carbon electrode rotated at 1500 rpm was used for rotating disk electrode measurements. Infrared spectra were collected on a MIDAC FTIR spectrometer. All pH values were measured on a Beckman ϕ -11 pH meter with a Markson combined electrode.

Cyclic voltammetry. Typically, a mixture of 5 ml of solvent/buffer and 100 μ l of a stock solution of NN (5.1×10^{-2} M in acetone) was added to a small (3 ml) voltammetric cell and the solution was purged with

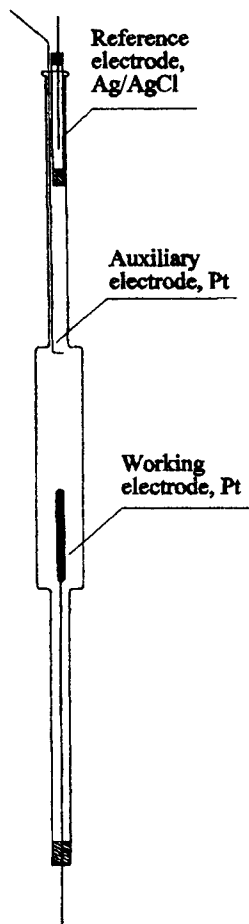


Figure 1. ESR cell with electrodes

nitrogen for 10 min. The selected potential range was scanned three times and the third scan used for data analysis. Before each measurement, the working electrode was polished on a polishing cloth with 0.005 μ m γ -alumina (Buehler) and distilled water by rubbing in a circular motion for 2 min. Peak potentials of the recorded voltammograms were determined as the potential at maximum current compared with the zero current line. For peak current measurement the extended charging current line preceding the peak was used as a baseline. A 0.1 M $\text{Cu}(\text{OAc})_2$ solution in acetic acid was used for complexation.

Chronocoulometric measurements. The number of electrons exchanged in the anodic oxidation of NN was determined using a 5×10^{-3} M solution of NN in 0.2 M NaHCO_3 -ethanol (1:1, v/v). The solution was purged with nitrogen prior to being injected into the cell. The potential was stepped from 0 to 500 mV and the charge vs time curve recorded. Using the same routine the curves were recorded with separate solutions of buffer alone, 5×10^{-3} M potassium hexacyanoferrate (II) and the NN solution. The cell was not opened for electrode polishing to preserve the thickness of the cell. The results were processed by extrapolating the linear part of the charge vs time curve to time zero and adjusted for the slight difference in charge at time zero ($Q = 0$ at $t = 0$).⁸

Rotating disk electrode (RDE) studies. A cell equipped with electrodes as in CV and containing 15 ml of solution was purged for 10 min with nitrogen. The buffer and solutions of the standard and sample were scanned in the same potential range (0 to 500 mV). Before each scan the working electrode was polished as described above. A sigmoidal current vs potential curve was obtained. The current increase was measured between lines extrapolated from linear portions of the curve before and after the change.

ESR. Solutions for ESR measurements were prepared and purged with nitrogen in a separate container. Solutions were 1×10^{-3} M NN in 0.2 M aqueous NaHCO_3 -ethanol (1:1, v/v) or 0.1 M TBAP in acetonitrile. The solution was inserted in an ESR cell equipped with the working electrode and a stream of nitrogen was passed over the solution. The remaining electrodes were inserted and the cell was sealed with Parafilm. When the cell was in the ESR spectrometer, the electrodes were connected to the potentiostat and the potential was applied. Spectra were recorded after a few minutes with the potential applied during all measurements. For half-life determinations spectra were taken after the current was turned off. In chemical oxidation experiments, excess solid lead tetraacetate was added to aqueous solutions of NN just prior to insertion of the sample in the ESR cavity.

Calculations. The Gaussian 92⁹ and Gamess series of programs were used for *ab initio* molecular orbital calculations. The restricted Hartree-Fock method was used for non-radical structures and the unrestricted HF method for radical species. All calculations were done using the 6-31 G basis set. Standard bond lengths and angles¹⁰ were used as the starting point for geometry optimizations of the two tautomeric forms of NN. These two geometries were then used as the starting point for all other structures investigated. Both NN tautomeric forms were found to be planar when no geometry restrictions were imposed. The same behavior was assumed for other structures and their ring systems were kept planar with constant dihedral angles.

RESULTS

CV scans in the potential range 0 to 1.0 V of NN solutions in aqueous buffers in the pH range 0.85–12.45 and in acetonitrile (AN) showed a quasi-reversible redox couple. Peak separations between 60 and 300 mV were measured for scan rates ranging from 2 to 500 mV s⁻¹. The electrochemical behavior of this couple was independent of electrode processes in other potential regions, since the potential range had no effect on the peak currents or shapes of the curves. The peak potentials E_{pa} and E_{pc} obtained in a series of aqueous buffer-ethanol (1:1) mixtures are shown in Table 1. A plot of redox potentials $[(E_{pa} + E_{pc})/2]$ vs pH is linear with a slope approximately -56 mV pH^{-1} , as expected for a one-electron, one-proton electrode process, up to the polarographic pK_a of 7.41 for NN, in good agreement with literature values.¹¹ For pH values higher than the pK_a value the effect on the peak potentials is negligible.

Thin-layer cell chronocoulometry and RDE voltammetry in a pH 8.7 buffer-ethanol mixture provided data

Table 1. Peak potentials vs pH for $1 \times 10^{-3} \text{ M}$ NN solutions in aqueous buffers

Peak potential	pH					
	1.5	3.5	6.0	8.0	10.0	12.0
E_{pa} (mV)	829	688	555	460	433	433
E_{pc} (mV)	678	590	437	355	334	336

on the number of electrons corresponding to the NN oxidation. Both techniques, with hexacyanoferrate (II) for calibration, gave the same value of 0.94 electron per NN molecule.

CV in the potential range -1.0 to $+1.5 \text{ V}$ at a scan rate of 200 mV s^{-1} of NN solution in AN in the presence of TBAP as supporting electrolyte showed a redox couple with peak potentials E_{pa} and E_{pc} of 852 and 560 mV, respectively. Similarly to the aqueous medium, the redox couple behavior is independent of redox processes in other potential regions.

Electrooxidation of NN in an ESR cell at 1.0 V

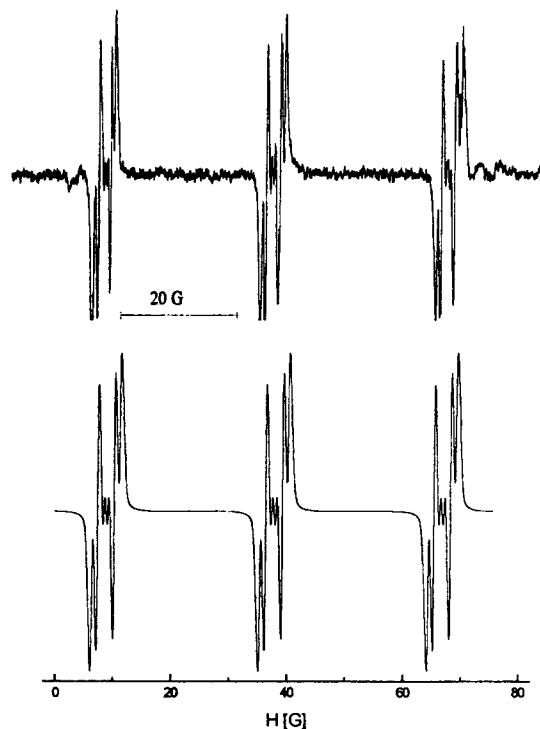


Figure 2. ESR spectrum of electrogenerated NN radical from a saturated solution of NN in 0.2 M NaHCO₃ in D₂O, with applied voltage of +1.0 vs Ag/AgCl. Observed (top) and simulated (bottom) spectra

Table 2. ESR data obtained by electrooxidation of NN in aqueous ethanol^a and acetonitrile solutions

$g \pm 0.0002$	a_N (G)	a_H^b (G)	$t_{1/2}$ in H ₂ O ^c (s)	$t_{1/2}$ in AN ^c (s)
2.0067	29.0 ± 0.1	2.91 ± 0.01 1.23 ± 0.01 0.88 ± 0.01	150 ± 18	3600 ± 120

^a 1:1 mixture of 0.2 M NaHCO₃ and ethanol.

^b See text for assignments.

^c Ambient probe temperature.

Table 3. Selected bond lengths and relative energies from *ab initio* calculations for NN and related radicals

Compound ^a	Relative energy (kcal mol ⁻¹)	Bond length (Å)			
		C-1—N	C-2—O	C-1—C-2	C-3—C-4
NN (p)		1.39	1.34	1.39	1.36
NN (q)	0.5 vs NN (p)	1.28	1.24	1.48	1.33
NN ^{••} (p)		1.34	1.30	1.47	1.37
NN ^{••} (q)	35 vs NN ^{••} (p)	1.29	1.34	1.46	1.39
NN [•]		1.35	1.29	1.45	1.38
NN ⁻		1.36	1.25	1.44	1.34

^a (p) and (q) denote phenolic and quinonoid forms, respectively.

provided a strong triplet with additional hydrogen hyperfine splitting (Figure 2). Hyperfine splitting constants for hydrogens were obtained from best-fit simulations.¹² When the circuit was opened, the ESR peak intensities decayed exponentially with time, allowing calculation of half-life times. Hyperfine splitting constants and half-life time values for radicals in aqueous and acetonitrile solutions are shown in Table 2. Replacing water with deuterium oxide had no effect on the splitting pattern. A similar ESR spectrum was obtained by oxidation of NN with lead tetraacetate in aqueous solution.

To examine the effect of complexing metal ions on the one-electron redox process, CV scans were made in aqueous NN solutions with various amounts of copper(II) acetate. With increasing concentration of copper ions the current of the quasi-reversible couple of NN decreased, and the peak was absent in the presence of excess Cu(II).

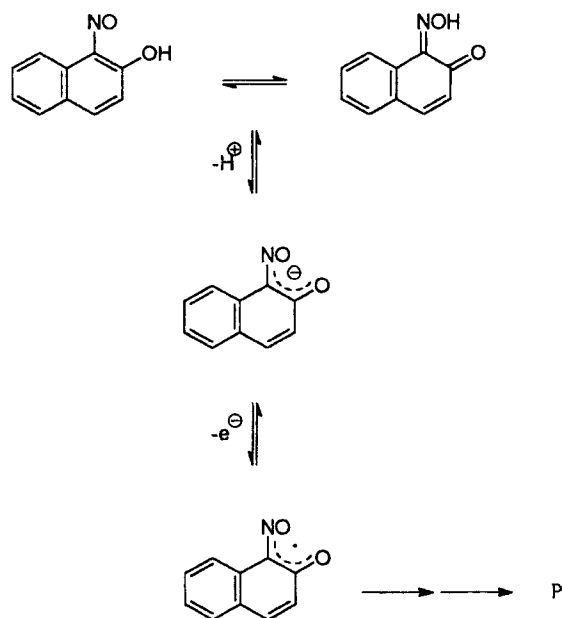
Ab initio MO calculations were carried out on both NN tautomers and related radicals. Results of the calculations, which do not include solvent interactions, on both tautomers, their radical cations, the iminoxyl radical and the anion of NN are given in Table 3.

The data show that the nitrosophenol form has 0.5 kcal mol⁻¹ lower energy than the quinone monooxime form. Such a difference is not significant and both forms have virtually the same energy in the absence of solvent. Spectroscopic studies support this result, since an equilibrium mixture was reported for NN in various solvents,¹³ with the phenol favored in aprotic media and the quinone monooxime form in protic solvents. The important point resulting from these calculations is that there is no significant effect from aromatic stabilization, and any preference in the tautomeric equilibrium should be attributed to other interactions, especially with the solvent. When optimized geometries for the nitrosophenol and quinone monooxime were used as input data for NN radical calculations, the same structure was obtained in both cases. A similar result was obtained in calculations on the NN anion. These results thus predict only one radical and one anion form. The NN radical cation, on the other hand, is predicted to exist in two tautomeric forms with the nitrosophenol form lower in energy by 35 kcal mol⁻¹.

DISCUSSION

The reported anodic oxidation study of NN using solid electrodes complements previous polarographic reduction studies. A quasi-reversible redox couple was observed by CV in the potential range 0 to 1.0 V vs Ag/AgCl, both in a wide pH range in water-ethanol and in acetonitrile solutions. No film was formed on the electrode under any conditions. In aqueous medium, the pH dependence indicates an electrode mechanism involving a one-electron, one-proton process. The one-electron mechanism is further corroborated by results from chronocoulometry and RDE voltammetry.

The electrochemical studies and MO calculations suggest the following scheme for electrochemical oxidation of NN:



Only a single resonance hybrid exists for both the NN anion and radical, since calculations converge on only

one structure regardless of whether the structure of the oxime or the phenol was used for the input. There is no evidence of the preceding tautomeric equilibrium on the voltammetric behavior of NN. The fast proton exchange preceding electron transfer is evident from the peak potential dependence on pH.

The voltammetric behavior and the presence of a strong ESR signal and its slow decay show that a relatively stable radical is generated in the NN oxidation. The large nitrogen hyperfine splitting of 29 G indicates that the product is an iminoxyl σ -radical.¹⁴ Generation of the radical in H₂O and D₂O showed identical ESR splitting patterns and hyperfine splitting constants for the radical. This observation suggests that no exchangeable hydrogens, such as the hydroxy or oxime hydrogen, are present to split the signal and that the radical is a neutral species. Nitrogen splitting was reported for radicals generated from NN by oxidation with silver(II) complexes⁴ and by irradiation of a hydrogen peroxide solution.^{5a}

Computer simulation produced an ESR spectrum that showed splitting by three different hydrogens (a_H values 2.91, 1.23 and 0.88 G) in addition to the nitrogen. The hydrogen adjacent to the hydroxy group is most likely causing the largest hydrogen splitting (2.91 G), due to a W structural pattern¹⁵ with the lone electron localized on the nitrogen atom. Hydrogens in positions 4 and 8 cause the additional splitting, although it is uncertain which to assign to the 1.23 and which to the 0.88 G HFS. H-4 is most likely interacting through bonds, whereas H-8 interacts 'through space' as commonly seen with iminoxyl radicals.¹⁵ The splitting of the signal by ring hydrogens shows that even though the radical is classified as a σ -radical, the unpaired electron interacts with the π -system. The magnitude of the present a_N (29 G) is further evidence for the neutral iminoxyl as the persistent radical rather than the cation radical. Spin densities (ρ) for these species were used to calculate a_N by the equation¹⁶ $a = C\rho$, where C is the proportionality constant specific for an atom.¹⁷ The predicted value of 23.7 G for the neutral form is close to that observed, whereas that for the cation radical (0.5 G) is too low. Additional evidence for the neutral iminoxyl radical is found in the experimental g value of 2.0067, which is in accord with values reported for other iminoxyl radicals and higher than those of radical cations (2.0007).²

The electrochemically generated radical was found to be relatively stable in aqueous media ($t_{1/2} = 150$ s), and its stability increased substantially in aprotic acetonitrile ($t_{1/2} = 3600$ s). The relatively long radical lifetimes in the present study indicate a stabilizing effect of a vicinal carbonyl function, since in the absence of this group similar radicals of aromatic nitroso compounds have substantially shorter lifetimes.³ The stabilizing effect of the carbonyl group is further supported by the report of long lifetimes of

radicals derived from 1,3-dione-2-oxime compounds.^{5b} The present results indicate that the decay of the electrochemically generated radical is relatively slow and is first order in the radical species.

The absence of the quasi-reversible couple in the presence of excess Cu(II) ions shows that metal complexation¹⁸ prevents the formation of a stable radical.

CONCLUSION

While most electrochemical studies of nitroso compounds have concerned their reduction, the present study has shown that electrooxidation of NN produces an unusually stable neutral iminoxyl radical. Support for this radical is based on a one-electron oxidation process as determined by chronocoulometry and RDE experiments and the pH dependence of peak potentials by CV. The iminoxyl radical was further characterized by its ESR spectrum, which showed a nitrogen hyperfine splitting constant of 29.0 G, typical of iminoxyl radicals.

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