

Oxidation of Aniline Dimers in the Electrospray Emitter

Keiji Asano¹, Haiteng Deng², Vilmos Kertesz¹, Gary Van Berkel¹

¹Oak Ridge National Laboratory, Oak Ridge, TN 37831-6365

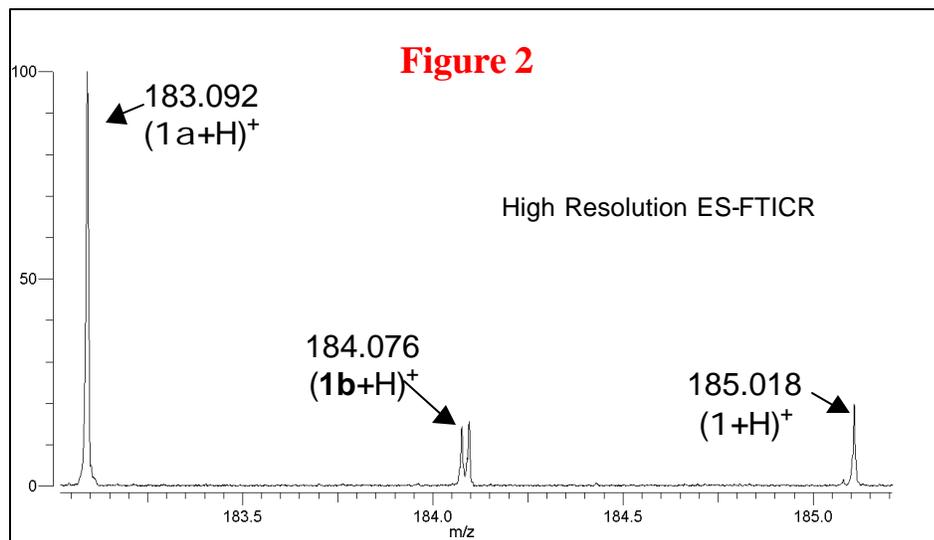
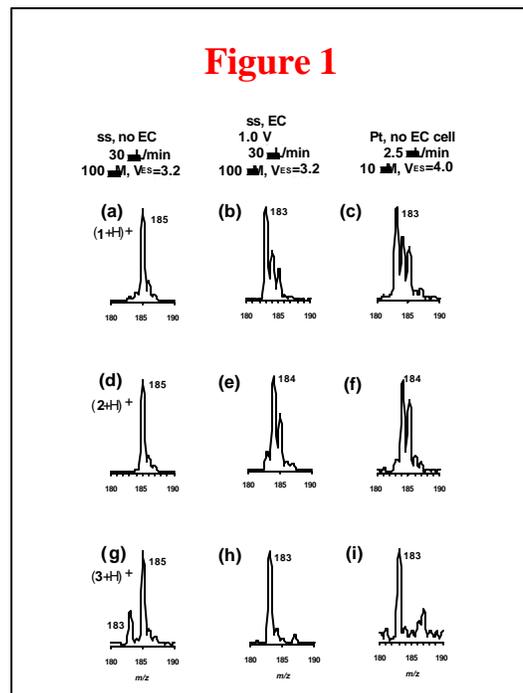
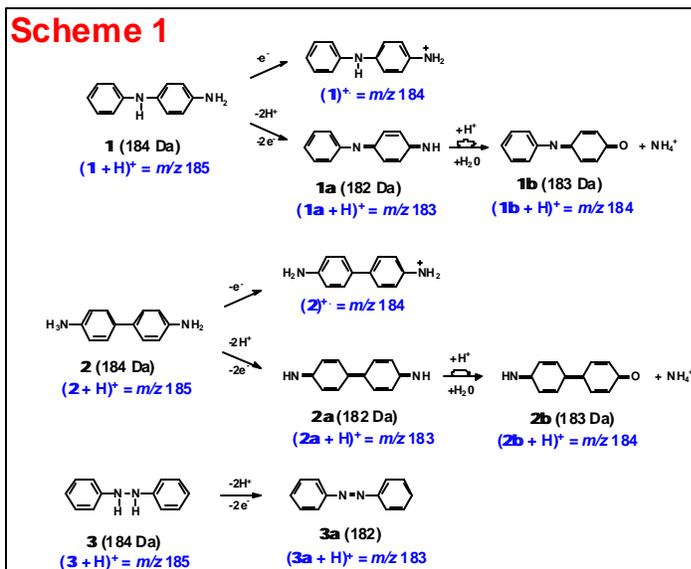
²Albert Einstein College of Medicine, Bronx, NY 10461

In this work, we report on using the controlled-current electrolytic nature of the electrospray (ES) ion source (1) to study oxidation of aniline dimers under various ES mass spectrometry (ES-MS) operating conditions. The structure of the head-to-tail (HT, 1), tail-to-tail (TT, 2), and head-to-head (HH, 3) linked dimers studied are shown in Scheme 1. We have previously studied oxidation of these compounds using a thin-layer electrochemical cell on-line with ES/MS (EC/ES-MS) (2). In those EC/ES-MS studies, operational parameters were chosen to minimize the impact of the ES electrolytic phenomenon on the electrolysis products formed in the upstream on-line cell.

Experiments were performed on either a PE Sciex API 365 (triple quadrupole) equipped with a "Turbo Ion Spray" ES ion source or a 7 Tesla Ion Spec ES-FTICR instrument. Solutions of dimers 1, 2, and 3 were prepared just prior to analysis to avoid any oxidation by exposure to air and light. Samples were prepared in 1/1 (v/v) H₂O/CH₃OH, 0.75% HOAc and 5 mM NH₄OAc. Solutions were continuously infused through one of two metal capillaries, a 100 μm i.d. stainless steel capillary or a 100 μm i.d. platinum capillary (both 3.5 cm, 400 μm o.d.). Flow rates and the applied ES potential (V_{ES}) were varied and the resulting mass spectra recorded. Electrospray currents were measured by grounding the curtain gas plate through a Keithley electrometer.

Figure 1 compares the ES mass spectra of the aniline dimers obtained with a stainless steel capillary (a,d,g), a stainless steel capillary with an upstream on-line electrochemical cell (b,e,h) both under conditions where the analyte electrolysis in the emitter is minimized (high flow rate, low V_{ES}), and with a platinum capillary at low flow rate and high ES potentials (V_{ES}) where electrolysis in the emitter is maximized (c,f,i). The major oxidation products are observed at m/z 183 and m/z 184 whether formed in the on-line cell or in the ES emitter. Compound 3, hydrazobenzene, the head-to-head dimer, is oxidized to form exclusively 3a by a two electron, two proton transfer process, which is observed as the protonated molecule (3a+H)⁺ at m/z 183. Compound 1, *N*-phenyl-1,4-phenyldiamine, the head-to-tail dimer forms two oxidation products, one at m/z 183, (1a+H)⁺, and the other at m/z 184. High resolution data (Figure 2) shows that there are two species with nominal m/z 184. One, m/z 184.099, is the isotope peak of the main product at m/z 183, and the other, m/z 184.076, is the product of hydrolysis of that same imine viz., (1b+H)⁺. Compound 2, benzidine, is the tail-to-tail dimer. The major oxidation product is observed at m/z 184. We believe this product is the hydrolysis product (2b+H)⁺. It would be unusual for the radical cation, (2)⁺, to survive long enough in this aqueous solvent to be detected, and imines (like 1a also) readily hydrolyze in H₂O. It is possible that the species observed at m/z 184 that is formed in the ES capillary is different than that formed in the EC cell. High resolution, which would confirm the identity of these species, have not yet been obtained.

A series of experiments were performed to determine conditions for maximized oxidation of the aniline dimers in the ES capillary. Generally, the greatest extent of oxidation occurred at low flow rates and higher V_{ES} . Easily oxidized compounds (3) show good electrolysis efficiency with both platinum and stainless steel emitters at low flow rates. For less readily oxidized species (1 and 2), the difference in oxidation efficiency between the two capillaries becomes more apparent with increasing flow rates. Higher flow reduces the electrolysis time and thus electrolysis efficiency. Because the stainless steel capillary can corrode, the current available for analyte oxidation is diminished. This combination (less current, less electrolysis time) manifests itself in the more apparent differences between stainless and platinum capillaries for the oxidation of HT and TT dimers.



- (1) Van Berkel, G.J.; Zhou, F. *Anal. Chem.* **1995**, *67*, 2916-2923.
(2) Deng, H.; Van Berkel, G.J. *Anal. Chem.* **1999**, *71*, 4284-4293.

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