

## Final Report

**Project Title:** "Studies Related to Chemical Mechanisms of Gas Formation in Hanford High-Level Wastes" (Award No. DE-FG07-96ER14690)

**Principal Investigator:** E. Kent Barefield  
School of Chemistry & Biochemistry  
Georgia Institute of Technology  
Atlanta, GA 30332-0400  
404-894-4034  
kent.barefield@chemistry.gatech.edu

**Co-Investigators:** Charles L. Liotta  
School of Chemistry & Biochemistry  
Georgia Institute of Technology  
Atlanta, GA 30332-0400  
404-894-8885  
charles.liotta@chemistry.gatech.edu

Henry M. Neumann  
School of Chemistry & Biochemistry  
Georgia Institute of Technology  
Atlanta, GA 30332-0400  
404-894-4033

**Co-Workers:** Anthony Belcher, Ph.D. 2001  
Sean Seymore, M.S. 1996  
Gregory Lavaty, graduate student (1998-99)  
Candice Halbert, graduate student (summer 2001)  
Liz Meazell, undergraduate student (summer, fall 1999)  
Carrie Young, undergraduate student (spring 2000)  
Vikram Kumar, post-doctoral (1997-98, eight mon.)

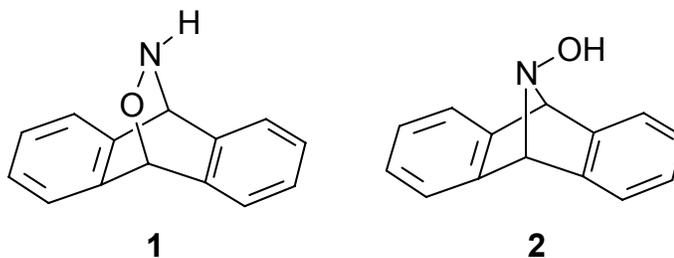
## Research Objective

The objective of this work is to develop a more detailed mechanistic understanding of the thermal reactions that lead to gas production in certain high-level waste storage tanks at the Hanford, Washington site. Prediction of the combustion hazard for these wastes and engineering parameters for waste processing depend upon both a knowledge of the composition of stored wastes and the changes that they undergo as a result of thermal and radiolytic decomposition. Since 1980 when Delagard<sup>1</sup> first demonstrated that gas production ( $H_2$  and  $N_2O$  initially, later  $N_2$  and  $NH_3$ ) in the affected tanks was related to oxidative degradation of metal complexants present in the waste, periodic attempts have been made to develop detailed mechanisms by which the gases were formed. These studies have resulted in the postulation of a series of reactions<sup>2</sup> that account for many of the observed products, but which involve several reactions for which there is limited, or no, precedent. For example,  $Al(OH)_4^-$  has been postulated to function as a Lewis acid to catalyze the reaction of nitrite ion with the metal complexants,  $NO^-$  is proposed as an intermediate, and the ratios of gaseous products may be a result of the partitioning of  $NO^-$  between two or more reactions. These reactions and intermediates have been the focus of this project since its inception in 1996.

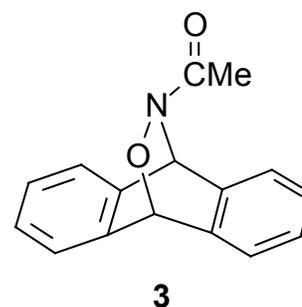
## Research Progress and Implications

The primary focus of this 60 mon (three years plus two twelve-month no-cost extensions) project has been toward (1) the development of precursors that would allow  $NO^-$  to be generated rapidly and under controlled conditions, (2) further development of models for aluminum catalyzed nitrite oxidation of HEDTA, and (3) an analysis of the relative contributions of thermal vs radiolytic pathways for complexant decomposition in tank 101-SY. All efforts since the previous report have been devoted to tasks (1) and (2) the major results of which will be briefly described below.

(1) Precursors to  $NO^-$ . The anion  $NO^-$  has been proposed, based upon extensive chemical investigations of models, as a key intermediate in the thermal generation of gases in tank wastes. However, this anion has only been conclusively identified only in the gas phase and information on the chemical behavior of the species in condensed phases is based solely upon indirect evidence; there have been no direct observations of the anion. A major objective of this research was the development of a precursor that would allow generation of  $NO^-$  at a sufficient rate that it could be identified spectroscopically (vibrational, emission) or by chemical trapping under controlled conditions. Attempts to increase the reactivity of Piloty's acid by synthetic modification were previously reported. More recent efforts were directed toward the utilization of known<sup>3</sup> anthracene derivative **1** for this purpose and toward the synthesis of anthracene derivative **2** as an alternative precursor.

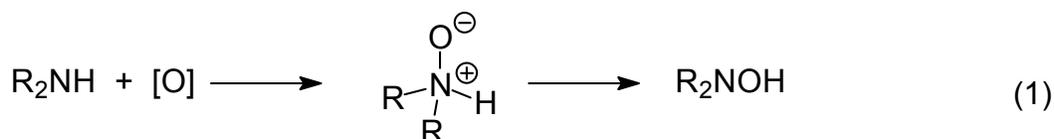
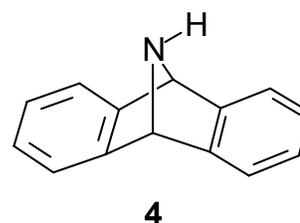


An improvement on the literature synthesis of **3**,<sup>4</sup> the precursor to **1·HCl**,<sup>3</sup> and to the starting 9,10-dimethylantracene (DMA) (previously reported) made **1** conveniently available for study under a variety of conditions. The relative ease with which **1** can be manipulated in solution at, or somewhat above, room temperature suggested that thermal decomposition was not likely to be a useful means for generating NO<sup>-</sup> (via reaction of HNO with base). PM3 calculations indicate the enthalpy of this reaction to be 17.1 kcal mol<sup>-1</sup> in the gas phase.<sup>3</sup> That thermal decomposition was quite slow was confirmed for several solvents. Photochemical decomposition of **1** (Hg lamp) was not significantly faster than the thermal reaction in THF or CHCl<sub>3</sub>.



The conjugate base of **1**, **1-H** was generated under a variety of conditions using strong bases (THF, BuLi, BuLi/TMEDA, NaH; DMSO, BuLi, Nadimsyl) and attempts made to monitor its stability by the evolution of fluorescence of the DMA product. The reaction in THF was slow ( $t_{1/2} > 1$  day) under all conditions. That the reaction had proceeded as expected was strongly suggested by the precipitation of M<sub>2</sub>N<sub>2</sub>O<sub>4</sub> (M=Li, Na) after several days. Combination of base with **1** in DMSO resulted in the very rapid formation of a dark green color, but variable levels of fluorescence. Ultimately, it was determined that the dark green color was most likely due to the radical anion of DMA and that it was responsible for quenching of fluorescence of DMA. Because it was very difficult to obtain **1** totally free of DMA, it was difficult to accurately determine the course of these reactions and these attempts were ultimately abandoned. M<sub>2</sub>N<sub>2</sub>O<sub>4</sub> was isolated from spent solutions after a few days, which again strongly suggests that the desired reaction had occurred albeit at an unknown rate.

Efforts to synthesize **2** from the known secondary amine **4**<sup>5</sup> were undertaken concurrently with the studies of **1**. There are two basic strategies for the conversion of secondary amines to hydroxyl amines. The first relies upon addition of an oxygen atom to the amine lone pair, followed by tautomerization to the hydroxyl amine (1)



The second relies upon addition of OX to the nitrogen lone pair followed by conversion of the N-O-X bond to NOH. The most common version of this reaction involves the use of acylperoxides, as illustrated (2).

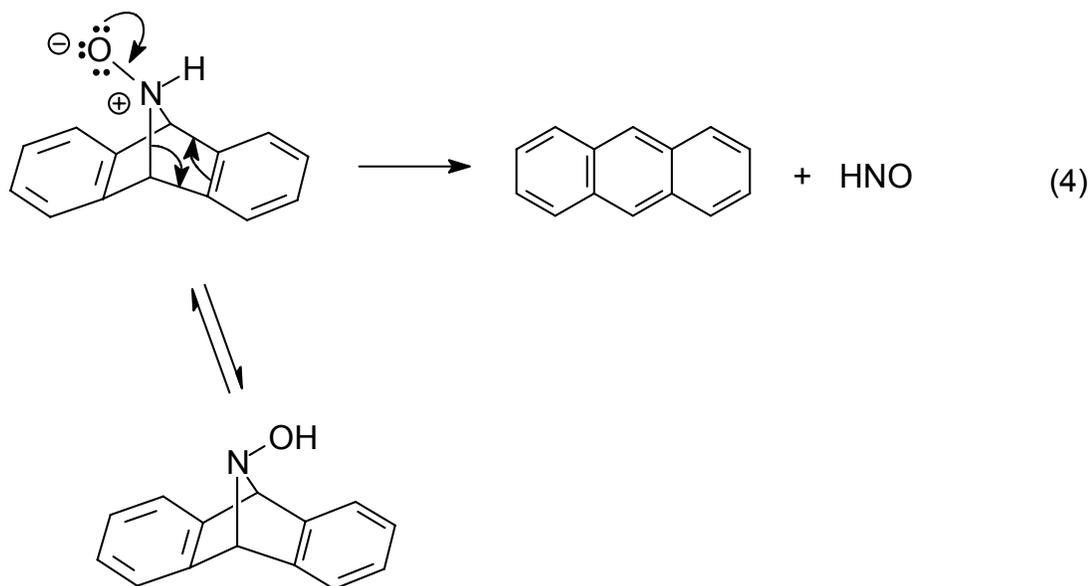


A third possibility explored in this work is the reaction of haloamine with acylates (3).



Hydrolysis as in (2) would liberate the hydroxyl amine.

Reagents utilized for the first reaction include  $H_2O_2$ , m-chloroperbenzoic acid, Caro's acid and methylrheniumtrioxide/ $H_2O_2$ . In almost every instance, except one *vide infra*, **4** was converted more or less rapidly to anthracene (>90%). This reaction was slowest for dilute hydrogen peroxide and fastest for the methylrheniumtrioxide (MTO) catalyzed oxidation with hydrogen peroxide (aqueous solution, or urea adduct - UHP). When the latter reaction was run in a closed system the headspace contained  $N_2O$ , consistent with the formation of  $HNO$ , which is known to decompose to  $N_2O$  via the dimer,  $H_2N_2O_4$ . This strongly suggests that the major reaction pathway for reactions that generate amine oxide as intermediate decompose according to (4):

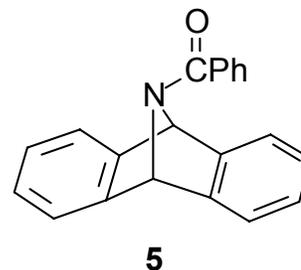


Cheletropic loss from the N-oxide is not without precedent as Gribble<sup>6</sup> has shown that the N-methyl tertiary amine loses nitrosomethane upon oxidation. Apparently loss of  $HNO$  is faster than tautomerization to the hydroxyl amine, or the tautomerization reaction is reversible, at least under the reaction conditions. We have been unsuccessful in finding any literature pertaining to the position of the amine oxide=hydroxyl amine or the rate of interconversion.

When the MTO/ $H_2O_2$  reaction with **4** was conducted at low temperature an unknown bicyclic anthracene adduct was detectable along with anthracene in a 1:2 ratio. It is our hypothesis that this may be the desired hydroxylamine. Unfortunately all attempts to increase the proportion of this species or to isolate it have thus far failed.

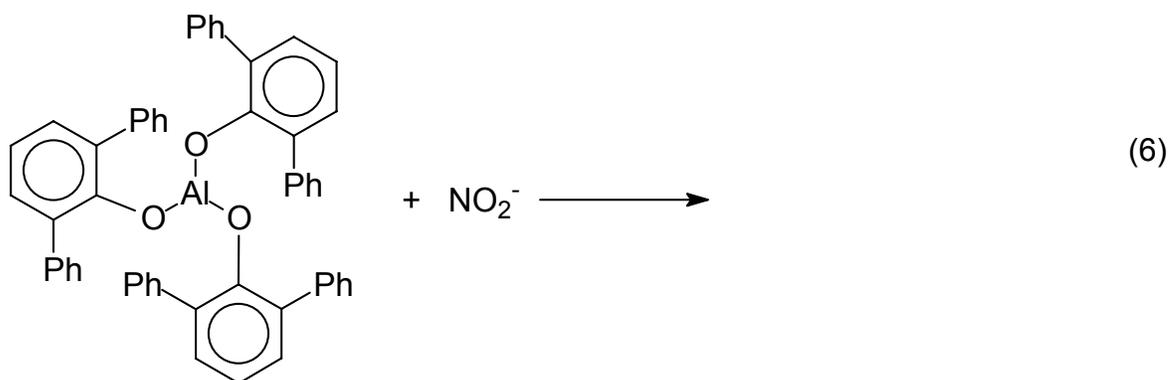
Reaction of **4** with benzoyl peroxide under basic conditions as outlined by

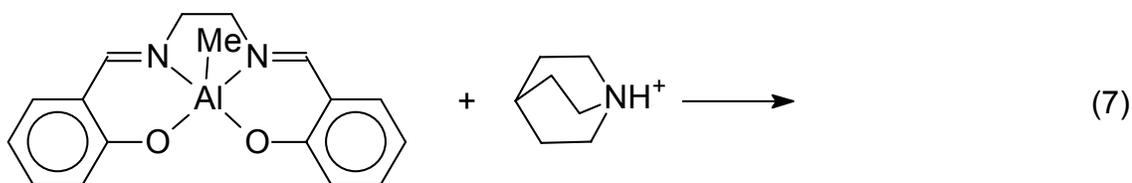
Biloski<sup>7</sup> proceeded slowly and yielded only benzamide **5**. Operating under the premise that perhaps the nucleophilicity of **4** was low and that this affected the selectivity of the reaction, the conjugate base **4-H**, previously synthesized by Cummins,<sup>8</sup> was used in reactions with benzoyl peroxide. A more rapid reaction occurred but the product was still **5**.



Several attempts were made to utilize the N-bromo derivative of **4** in reactions with metal carboxylates including sodium benzoate and silver and thallium acetates. Although both AgBr and TlBr were formed, the desired acyloxy derivatives of **4** were not detectable in the product mixtures. Further efforts to prepare **2** were abandoned.

(2) Models for aluminum catalyzed nitrite oxidation of HEDTA. Investigation of reactions of HEDTA in simulated wastes<sup>1,2c</sup> indicate that aluminum, which is present in the convective phase as  $\text{Al}(\text{OH})_4^-$ , catalyzes the reaction of nitrite with HEDTA (and other organics). It has been proposed<sup>2</sup> that this catalysis results from the formation of equilibrium amounts of a species such as  $\text{Al}(\text{OH})_3\text{ONO}^-$  that nitrosates basic sites in the organic thus initiates its “decomposition” and ultimately the formation of gases. Although model reactions involving Al(III) species and nitrite have been demonstrated capable of cleaving N-C bonds<sup>2c</sup> and coordination of  $\text{NO}_2^-$  by Al(III) suggested by NMR studies in acetonitrile<sup>2a</sup> no isolated, fully-characterized aluminum-nitrite species has ever been reported. We have attempted, albeit unsuccessfully thus far, to prepare an aluminum nitrite species in order to determine its structure and chemical reactivity. Reactions (5)-(7) have been attempted but characterizable products have yet to be obtained from any of the reactions. Studies in this area are continuing with alternative funding.





## References

- (1) Delagard, C.H. *Laboratory Studies of Complexed Waste Slurry Volume Growth in Tank 241-SY-101, RHO-LD-124, Rockwell Hanford Operations, Richland, WA, 1980.*
- (2) (a) "Mechanisms of Gas Generation from Simulated SY Tank Farm Wastes: FY 1995 Progress Report," Barefield, E.K.; Boatright, D.; Desphande, A.; Doctorovich, F.; Liotta, C.L.; Neumann, H.M.; Seymore, S. PNNL-11247, **1996.**  
 (b) "Mechanisms of Gas Generation from Simulated SY Tank Farm Wastes: FY 1994 Progress Report," E.K. Barefield, D. Boatright, A. Desphande, F. Doctorovich, C.L. Liotta, H.M. Neumann, and S. Seymore, PNL-10822, **1995.**  
 (c) "Synthetic Waste Chemical Mechanism Studies," E.C. Ashby, A. Annis, E.K. Barefield, D. Boatright, F. Doctorovich, C.L. Liotta, H.M. Neumann, A. Konda, C.F. Yao, K. Zhang, and N.G. McDuffie, WHC-EP-0823, **1994.**
- (3) Kirby, G.W.; Sweeny, J.G. *J. Chem Soc., Perkin I* **1981**, 3250; Kirby, G.W.; Sweeny, J.G. *J. Chem. Soc., Chem. Commun* **1973**, 704.
- (4) Belcher, M.A. Ph.D. Thesis, Georgia Institute of Technology, 2001.
- (5) Carpino, L.A.; Padykula, R.E.; Barr, D.E.; Hall, F.H.; Krause, J.G.; Dufresne, R.F.; Thoman, C.J. *J. Org. Chem.* **1988**, *53*, 2565.
- (6) Gribble, G.W.; Allen, R.W.; Anderson, P.S.; Christy, M.E.; Colton, C.D. *Tetrahedron Lett* **1976**, *41*, 3673.
- (7) Biloski, A.J.; Ganem, B. *Synthesis Commun.* **1983**, 537.
- (8) Mindiola, D.J.; Cummins, C.C. *Angew. Chem. Int. Ed.* **1998**, *37*, 945.