

# **Environmental Management Science Program**

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## **Studies Related to Chemical Mechanisms of Gas Formation in Hanford High-Level Nuclear Wastes**

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## Studies Related to Chemical Mechanisms of Gas Formation in Hanford High-Level Nuclear Wastes

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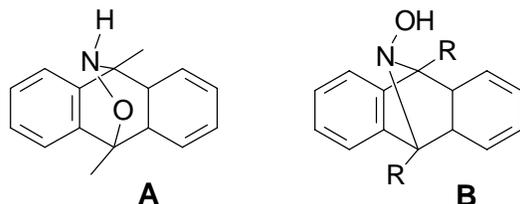
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### Research Objective

The objective of this work is to develop a 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

During the first 20 mon of this 36 mon project the primary focus 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.



(1) *Precursors to  $NO^-$*  (S. Seymore, A. Belcher, graduate students; V. Kumar, post-doctoral). The  $NO^-$  anion, like isoelectronic  $O_2$ , can exist in either the singlet state or the triplet state. Contrary to the considerable experimental and theoretical work on  $NO^-$  and its conjugate acids in the gas phase, relatively little is known about the anion in condensed phases although one theoretical study indicates that the triplet state is also the ground state of  $(NO \cdot 2H_2O)_{(g)}^{-3}$ . Our objective is to discover methods to rapidly generate  $NO^-$  in condensed phase under controlled conditions. To this end we have examined the thermal and photochemical reactions of **A**, neither of which occur sufficiently rapidly for our purposes. Studies on the anion of **A** are in progress.

Synthesis of **A** requires 9,10-dimethylantracene, which although commercially available, is very expensive. A low-cost, facile route to this compound and analogs based upon a nickel catalyzed

reaction between 9,10-dibromoanthracene and the appropriate Grignard reagent has been developed. These and other 9,10-dialkylated anthracenes are frequently used in photochemical and photophysics; the synthetic methodology will make these materials more accessible to a broad range of scientists.

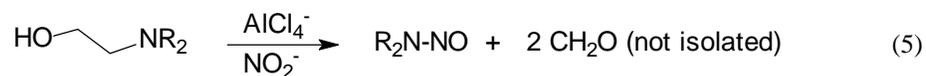
Good progress toward the synthesis of precursor **B** has been made, but the unexpected resignation of V. Kumar (post-doctoral) has temporarily halted this phase of the work. This work will resume as soon as a new postdoctoral or graduate student is identified for the project.

Thermal decomposition of Piloty's acid,  $\text{PhSO}_2\text{NHOH}$ , under basic conditions has long been believed to generate  $\text{NO}^-$ .<sup>4</sup> We have reexamined the kinetics of decomposition of this compound and the p- $\text{CF}_3$  derivative. These results suggest a more detailed mechanism for the decomposition of the mono anion than previously proposed (1)-(4).<sup>5</sup> Our results indicate that equilibrium amounts of the dianion,  $\text{PhSO}_2\text{NO}^{2-}$ , is formed at high pH ( $K_a \sim 10^{-14}$ ) and that it is unreactive compared to the monoanion. The monoanion of Piloty's acid was earlier suggested to be O-deprotonated based upon Overhauser enhancements in the nitrogen NMR spectrum.<sup>5</sup>



Although the presence of a second tautomeric form is not excluded by this interpretation we have attempted to acquire chemical evidence for the structure of the anion by alkylation experiments under basic conditions. After several unsuccessful attempts we now have preliminary evidence to suggest that alkylation of the anion of Piloty's acid is possible, but the structure of the alkylation product(s) has not yet been determined. It is anticipated that this will be accomplished within the next two months.

(2) *Development of models for aluminum catalyzed nitrite oxidation of HEDTA* (A Chalfant, undergraduate student). In simulated wastes HEDTA is cleaved by nitrite (aluminate is a necessary constituent) to ED3A, which is detected in real wastes. In earlier work<sup>2c</sup> C.-F. Yao determined that in acetonitrile a mixture of  $[\text{Et}_4\text{N}][\text{AlCl}_4]$  and  $\text{NaNO}_2$  cleaved model  $\beta$ hydroxyethyl amines in a similar fashion (5).



These reactions were slow, presumably because of the low solubility of  $\text{NaNO}_2$  in acetonitrile. One of these reactions,  $\text{R}_2 = -(\text{CH}_2)_5-$ , has been reinvestigated using  $[\text{Bu}_4\text{N}]\text{NO}_2$ , which is highly soluble in acetonitrile. Although not optimized it appears that more rapid reaction does occur. Gaseous products, which were not investigated in the earlier studies, will be determined by Ms. Chalfant during the next three months. Further NMR studies of the complexation of aluminum(III) by nitrite in acetonitrile solution<sup>2a</sup> will also be undertaken.

(3) *Analysis of the relative contributions of thermal vs radiolytic pathways for complexant decomposition in tank 101-SY*. A brief summary of the results of this analysis was given in the 1997 progress report. No further work has been done during the past 8 mon.

## References

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(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.  
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- (3) Roszak, S. *Chem. Phys. Lett.*, **1994**, 221, 255-258.
- (4) Bonner, F.T.; Ko, Y. *Inorg. Chem.* **1992**, 31, 2514.