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

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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 Delagard¹ 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 reactions² 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 32 months of this 48 month project (a 12 month extension has been requested) 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^- (A. Belcher, graduate student). 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 $(NO \bullet 2H_2O)_{(g)}^{-3}$. Our objective is to discover methods to rapidly generate NO^- in condensed phase under controlled conditions. Earlier attempts to thermally and photochemically decompose **A** indicated that neither reaction was sufficiently rapid for our purposes. Reaction of hydrochloride salt of **A** with 2 equiv of BuLi in THF yielded $Li_2N_2O_2$ but the reaction is relatively slow (hr). More promising are reactions of **A**•HCl in DMSO with dimsyl anion ($CH_3SOCH_2^-$), produced using BuLi or NaH, which appear to occur quite rapidly although the results have not been entirely reproducible. These reactions have been monitored using a colleague's spectrofluorometer, which is available only occasionally. An instrument has been ordered that can be devoted exclusively to this project.

We plan to examine the base induced decomposition of **A**•HCl in the presence of potential trapping agents (PhCHO, $Ni(CN)_4^{2-}$, dienes) for NO^- during the next few months. A manuscript describing a low-cost, convenient synthesis of 9,10-dimethylantracene, a precursor to **A**, is in preparation.

Methods to obtain NO^- by rapid electron transfer from strong reducing agents are under investigation. Possible reductants studied to date have included photochemically excited $\text{Ru}(\text{bipy})_3^{2+}$ in aqueous solution and sodium naphthalide in THF. Quenching of fluorescence of $\text{Ru}(\text{bipy})_3^{2+}$ was initially observed, but this was ultimately traced to impurities in the NO. In the course of this excursion, we discovered that the spectrum attributed to NO in aqueous solution⁴ is actually due to HONO. The products from the sodium naphthalide reaction are still under investigation, but the reaction is fast and most of the naphthalene can be recovered from the product mixture by sublimation.

A paper describing our study of the kinetics of decomposition of Piloty's acid (PhSO_2NHOH), a precursor for NO^- has been submitted for publication.⁵ As indicated in last year's report, our interpretation of the kinetics requires the participation of tautomeric forms of the monoanion of the acid. In view of the conclusion based upon Overhauser enhancements in the nitrogen NMR spectrum that the monoanion was O-deprotonated⁵ we attempted to acquire chemical evidence for the structure of the anion by alkylation experiments under basic conditions. We did obtain NMR spectral evidence to suggest that the anion could be trapped by alkylation with acrylonitrile, but the structure of the alkylated product could not be assigned directly by its NMR spectrum. Unfortunately attempts to independently synthesize the possible alkylated products failed and this approach was abandoned.

(2) *Development of models for aluminum catalyzed nitrite oxidation of HEDTA* (Greg Lavaty, graduate student). A focus of work in this area during the past year has been on the synthesis and study of aluminum nitrite compounds, which are currently unknown. Lavaty, a new graduate student in our group for six months during the year, did exploratory studies on the reaction of AlEt_3 with several reagents:

- (1) N_2O_3 in CH_2Cl_2 at $-20^\circ\text{C} \rightarrow$ no reaction
- (2) $\text{N}_2\text{O}_3 + \text{H}_2\text{O}$ in CH_2Cl_2 at -20°C gas evolution but the product was predominantly nitrate
- (3) $[\text{quinuclidineH}]\text{Cl}/\text{CH}_2\text{Cl}_2 + \text{AlEt}_3 \rightarrow$ gas evolution; apparently formation of $\text{quinuclidine}\bullet\text{AlCl}_3$
- (4) $[\text{quinuclidineH}]\text{Cl}/\text{CH}_2\text{Cl}_2 + \text{AgNO}_2 \rightarrow$ mixture of $[\text{quinuclidineH}]^+$ nitrite and nitrate

N_2O_3 was generated by passing gaseous NO through the CH_2Cl_2 solution of $\text{N}_2\text{O}_4/\text{NO}_2$ at -20°C to give the characteristic blue color. The results of reaction (2) suggest that conversion to HONO was not complete, if in fact, it actually occurs. A review of the literature is somewhat ambiguous on this conversion in condensed phases. Reaction (3) was done in preparation for the examination of the comparable reaction with the nitrite salt, which we anticipated making according to (4). Unfortunately several attempts at reaction (4) with multiple batches of both reagents has given products whose ^{14}N NMR spectra indicate gross contamination by nitrate. Exactly how nitrate is produced is unknown. Unfortunately Lavaty has left the graduate program; Further investigation of this chemistry will be undertaken by an undergraduate student during the summer.

(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 since.

References

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