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OCT 31 1997

The Honorable John T. Conway
Chairman, Defense Nuclear Facilities Safety Board
625 Indiana Avenue, N.W., Suite 700
Washington, D.C. 20004

Dear Mr. Chairman:

SUBJECT: Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 96-1 Implementation Plan - Report on Catalytic Decomposition of Soluble Tetraphenylborate (TPB) Studies

DNFSB Recommendation 96-1 Implementation Plan Milestone # 5.2.2-1 requires completion of laboratory studies on catalytic decomposition of soluble TPB. Enclosure 1, "Soluble Tetraphenylborate Decomposition Studies Status," summarizes the laboratory studies completed to date. These studies have identified palladium, coupled with benzene, diphenyl mercury, and decomposition intermediates, as the active catalyst system for decomposition of TPB and triphenylborane. Also, copper has been identified as the primary catalyst for decomposition of diphenylborinic acid and phenylboronic acid. Decomposition reaction rates under a range of conditions have been determined, but a statistical analysis of the rate constants has not yet been completed. Our current expectation is that the statistical analysis will be completed and the decomposition reaction rates fully documented by December 31, 1997. At that time, a complete report on catalytic decomposition of soluble TPB will be provided to you for closure of Milestone # 5.2.2-1.

Enclosure 1 has been previously discussed with your staff. Enclosures 2 through 9 are reference documents which have not been previously transmitted to you. Please direct any questions to me or W. F. Spader at (803) 208-7409.

Sincerely,

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Assistant Manager for
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ED:JWM:kl

PC-97-008

9 Enclosures

cc w/encl 1:
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Soluble Tetraphenylborate Decomposition Studies Status

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Soluble Tetraphenylborate Decomposition Studies Status

1.0 Summary

Studies to date have identified the active catalyst system for decomposition of tetraphenylborate (TPB) and triphenylborane (3PB) as palladium, in the presence of benzene, diphenyl mercury, and decomposition intermediates. Copper is the primary catalyst for diphenylborinic acid (2PB) decomposition and phenylboronic acid (1PB) decomposition. Factors which influence the decomposition have been identified. Decomposition reaction rates under a range of conditions have been determined. The most significant uncertainty remains with the benzene generation rate from the palladium-catalyzed reactions.

2.0 Background and Objectives

The In-Tank Precipitation (ITP) facility at the Savannah River Site initiated radioactive operation in Tank 48H in September of 1995. During pump operation in December of 1995, benzene evolved from Tank 48H at higher rates than expected, though the operational safety limit was never approached. Later investigations revealed the source of benzene was apparently from the catalytic decomposition of excess sodium tetraphenylborate (NaTPB) added to ensure adequate suppression of cesium solubility (reference 1).

In August 1996 the Defense Nuclear Facility Safety Board (DNFSB) issued Recommendation 96-1. The DNFSB recommended that operating and testing in the ITP facility not proceed without an improved understanding of the mechanisms of benzene generation, retention, and release. In the 96-1 Implementation Plan (reference 2), the Department of Energy developed its approach to resolve the issues raised by the DNFSB.

Implementation Plan Commitment # 3 states that an overall bounding benzene generation rate will be determined and documented based on the understanding of all major generation mechanisms. Milestone #5.2.2-1 provides the results of testing to understand catalytic decomposition of soluble TPB, including identification of primary catalysts, decomposition mechanisms and rate constants. This deliverable package provides the information acquired to date in support of milestone #5.2.2-1, identifies issues that have to be resolved before final closure of the milestone, and describes the path forward.

3.0 Approach

Activities to determine the primary catalysts and reaction mechanisms for soluble TPB-decomposition include three elements:

- develop and test an essentially complete simulant which produces decomposition rates similar to or greater than those observed in Tank 48H and provides the basis for further testing with simulants,
- perform tests to identify the primary catalyst or groups of catalysts, and
- perform tests to determine the primary reaction mechanisms and the rate constants for TPB decomposition including the intermediate reactions.

3.1 Objectives

The test objectives were designed to develop a more fundamental and quantitative understanding of the decomposition of soluble TPB and the consequent generation of benzene. Specific tasks described in the test plan (reference 3) were:

3.1.1 Perform tests to demonstrate a Tk 48H, Batch 1 simulant which produces rates similar to or greater than those observed in Tank 48H.

3.1.2 Determine significant reaction mechanisms and rate constants with soluble Cu catalyst as a function of temperature, hydroxide concentration, reactant and intermediates concentrations.

3.1.3 Perform preliminary testing to develop candidates for catalyst identification (ID) testing; include trace soluble species, sludge solids, sodium titanate, and organics.

3.1.4 Based on preliminary catalyst ID testing, perform statistically designed experiments to identify the primary catalyst(s).

3.1.5 Determine the effect of active catalysts on decomposition rates of TPB and the reaction intermediates.

3.1.6 Provide correlations and rate constants for use in modeling the decomposition reactions and the process flow sheet.

3.2 Test Approach

Testing was performed under three Task Technical Plans (TTPs) prepared by the performing organization. The TTPs contain detailed information on methods, temperatures, compositions, test conditions, and analytical requirements. The testing performed under each TTP is summarized below.

3.2.1 Decomposition Studies of Tetraphenylborate Slurries - C. L. Crawford (reference 4):

Tests using the Tk 48H, Batch 1 simulant (called the Enhanced Comprehensive Catalyst or ECC simulant) have the primary objective of demonstrating TPB decomposition rates similar to or exceeding rates observed in Tank 48H. The ECC simulant includes soluble salt components, soluble and insoluble NaTPB and KTPB solids, soluble metal ions, trace organic species, simulated sludge solids, and monosodium titanate (MST).

Tests were performed at three temperatures to determine the temperature dependence. The important parameters controlled were the starting simulant compositions and the test temperatures.

Testing of a scoping nature were also to obtain an early indication of the effect of removing insoluble solids from the salt solution. Slurries without sludge and/or MST were tested.

3.2.2 Sodium Tetraphenylborate Decomposition Catalyst Identification Studies - M. J. Barnes (reference 5):

Tests to identify catalysts were performed in phases. In phase one, preliminary tests were performed to define the best conditions (*e.g.* glass vs. carbon steel vessel, sealed vs. purged, agitated vs. unagitated) for performing subsequent statistically designed experiments. Phase one tests included 1) cross checks of two previous similar tests which produced different results, 2) tests using the Tk 48H, Batch 1 simulant at varying conditions to determine the best conditions for subsequent experiments, and 3) a screening test to determine if noble metals might be the principal catalysts.

For the second phase of preliminary tests, the effect of KTPB solids concentration and hydroxide concentration were examined. Tests also examined the effect of adding noble metals alone (no other ECC simulant components), and of adding MST and sludge solids in dehydrated form.

Based on the results of preliminary testing, the TTP was revised to specify the conditions for statistically designed tests of the ECC simulant recipe. These tests first identified the catalytic significance of major potential groups, including organic additives, trace soluble metals, and insolubles (sludge and MST). Active organic and active metal components were further tested to identify the specific catalyst composition. Additional tests were designed to examine the effect of Uranium and irradiation on the catalyst system.

3.2.3 Decomposition Studies of 3PB, 2PB, and 1PB in Aqueous Alkaline Solutions Containing Copper - C. L. Crawford (reference 6):

Decomposition Studies of 3PB, 2PB and 1PB in Aqueous Alkaline Solutions Containing Potential Catalysts - C. L. Crawford (reference 7):

Decomposition Studies of 3PB, 2PB, and 1PB in Aqueous Solutions Containing the Enhanced Catalyst Composition - W. R. Wilmarth and C. L. Crawford (reference 8):

The first step toward describing the TPB decomposition mechanisms and rate constants is to follow the decomposition of the intermediates in a simplified, "clean" system. Tests started with each intermediate (3PB, 2PB, and 1PB) in a statistically designed matrix to study the effects of temperature, NaOH concentration, and Cu concentration. Additional tests determined whether the components in the ECC simulants increased the decomposition above the rate with Cu only, and considered the effects of nitrogen compared to air atmosphere. Final tests addressed the effect of filtering solids out of the mixture.

4.0 Results

4.1 Tetraphenylborate Decomposition Studies

Tests of TPB decomposition with the ECC simulant showed that the simulant produced decomposition rates similar to those observed in Tank 48 (reference 9). The activation energy was lower than that calculated for Cu alone, suggesting the presence of an additional catalyst in the ECC system. It was observed that removal of the sludge solids reduced the catalytic activity. The testing reported in reference 9 supported continued experimentation with the ECC simulant for catalyst identification and additional decomposition studies. Preliminary statistical analysis of the TPB decomposition continue to indicate that the ECC simulant results in decomposition rates similar to those experienced in Tank 48 in December, 1995. This will be discussed further in the statistical analysis report.

4.2 Tetraphenylborate Catalyst Identification Studies

Preliminary catalyst ID tests (reference 10) confirmed the finding that TPB decomposition rates with the ECC simulant were reproducible and similar to those seen in Tank 48. No significant difference was observed between tests performed in carbon steel and glass vessels. A stirred system appeared slightly more reactive than an unstirred system. Tests containing only soluble TPB (no solid NaTPB or KTPB) were much less reactive than those containing solids. A strong dependency on sodium concentration was observed, with tests at 5.6 M Na+ approximately two orders of magnitude faster decomposition than those at 2.7 M Na+. Tests performed with only noble metals and no other ECC components did not show significant reaction.

The second set of preliminary tests (reference 11) showed that tests with all ECC components except the noble metals were not reactive, implicating at least one noble metal as part of the catalyst system. Further testing of KTPB solids showed that they were necessary for the reaction, but there was not a concentration dependency. The effects of dehydrated MST and sludge were insignificant. The rate effect observed at varying salt solution concentrations was due to the sodium rather than the hydroxide concentration. These results of the preliminary tests allowed the conditions to be set for subsequent testing.

Phase A of the statistically designed catalyst identification tests (reference 12) showed that both suspect active organics (benzene, 3PB, 2PB, 1PB, and diphenyl mercury) and metals (palladium, ruthenium, rhodium and silver) played a role in the catalyzed reaction. Copper did not promote a significant reaction relative to the reaction of suspect active organics and metals. Phase B of the statistically designed tests (reference 13) showed that all three suspect active organic classes (benzene, diphenyl mercury, and one or more of the decomposition intermediates) are required for the reaction to proceed. Phase C identified Palladium as the active metal catalyst. Phase D (reference 14) testing showed that uranium is not a catalyst and does not accelerate the catalyzed reaction. Neither pre-irradiation nor continuous irradiation accelerated the reaction; in fact, irradiation appeared to inhibit the reaction.

4.3 Intermediate Decomposition Studies

Initial studies (reference 15) of decomposition rates of intermediates (3PB, 2PB and 1PB) showed that 2PB and 1PB decomposed at similar rates in the presence of copper only, with the ECC simulant and in Tank 48. The decomposition rates increased significantly with increasing temperature. Decomposition of 2PB and 1PB showed dependency on the concentration of copper. Dissolved oxygen in the solution also appeared to affect the rates. The decomposition rate of 3PB was significantly lower with copper only than had been observed in Tank 48, suggesting the existence of another catalyst for 3PB.

Studies of the effects of dissolved oxygen on the intermediate decomposition rates (reference 16) showed that all three intermediates decomposed more slowly in inerted systems than in the presence of air. Benzene formation was favored in the inerted systems, whereas phenol formation was favored when the decomposition occurred in air. Rates of decomposition with the ECC simulant (which contains copper) were studied for comparison to the rates with copper only. Decomposition of 3PB occurred approximately three times faster with the ECC simulant than with copper, while the rates for 2PB and 1PB did not change. Rate constants for the decomposition of 2PB and 1PB in flowing air with a copper catalyst system were reported in reference 17.

5.0 Conclusions and Their Application

The following conclusions are drawn from these studies:

- copper (soluble) catalyzed decomposition of soluble TPB is occurring,
- copper (soluble) catalyzed decomposition of the soluble intermediates (3PB, 2PB, and 1PB) is also occurring,
- these copper catalyzed reactions are classic homogeneous catalysis reactions and are dependent upon the catalyst (copper) concentration, the concentration of the organic species of interest (TPB, 3PB, 2PB, or 1PB), and the ionic strength of the solution (the sodium or hydroxide concentration)
- the presence of oxygen (in solution) increases the rate of reaction (by oxidizing the copper (I) produced in the reaction back to copper (II),the active soluble form),
- the presence of oxygen (in solution)also shifts the product ratio from mostly benzene to mostly phenol,
- phenol production is not credited in the determination of benzene generation rates for the Authorization Basis (100% benzene production is assumed),
- palladium catalyzed reactions for the decomposition of TPB and 3PB is also occurring, these reactions are complex and require the presence of KTPB (organic solids), diphenyl mercury, benzene and at least one of the intermediates (the specific key intermediate was not determined),
- the requirement for these key components are not explained by the classic homogeneous catalyzed reaction, and has (when coupled with the latest results from the solids decomposition and real waste programs) resulted in questioning the mechanism for the palladium catalyzed reactions (see Additional Scope)
- removal of the organic and sludge solids from the system indicates a much slower decomposition rate (see Additional Scope), the resulting benzene generation rate will be applied to Tank 50 and the Salt Solution Hold Tank (SSHT) in the saltstone facility
- the data resulting from these studies provides an excellent database from which to determine the benzene generation rates for application to Tanks 48 and 49 under a variety of conditions, however the variability of the results requires a rigid statistical approach to the determination of the benzene generation rates (see Additional Scope)

5.1 Additional Scope

The above work was performed to support the determination of benzene generation rates in the ITP facility. Based on the results observed, separate decomposition rates will be applied for Tanks 48 and 49 (both of which contain KTPB and sludge solids) and for Tank 50 and Saltstone tanks (from which the KTPB and sludge solids have been removed through filtration). Additional scope was added to the original set of TPB and intermediate decomposition studies when it was observed that the presence of KTPB, NaTPB and sludge solids affected the decomposition rates.

The additional studies to determine the decomposition rate following removal of the sludge and organic solids by filtration are nearing completion. These studies have indicated a significant reduction in the rate of both TPB and 3PB decomposition following filtration. The results will be documented shortly.

The overall benzene generation rate is a function of the combined decomposition rates of TPB and each intermediate. The rate constant (assuming the homogeneous catalyzed reaction hypothesis) for each of these reactions (copper catalyzed decomposition of TPB, 3PB, 2PB, 1PB, and palladium catalyzed decomposition of TPB and 3PB) have been determined for each test conducted. As seen in the referenced reports these rate constants vary in proportion to the temperature, ionic strength, and catalyst concentration. To provide meaningful estimates of the bounding overall generation rate it is necessary to perform rigid statistical analysis. The statistical analysis has begun. It is anticipated that the individual test rate constants will then be regressed as a function of 1/Temperature (°K) (to provide an estimate of the activation energy) and the other key parameters which affect the rates (e.g. ionic strength, Pd concentration). This analysis will be completed and documented shortly.

The preliminary statistical analysis has indicated a degree of variability that could not be explained by the controlled variables. Additional work has been initiated to determine whether an additional variable affects the results or whether the reaction mechanism hypothesis for the palladium catalyzed decomposition reactions is incorrect. This work will provide the decomposition rate for the palladium-catalyzed reactions.

6.0 Path Forward

Studies to date have identified the active catalyst system for decomposition of TPB, as well as catalysts for each subsequent decomposition step. Factors which influence the decomposition have been identified. Decomposition reaction rates under a range of conditions have been determined and statistical analysis begun. A number of observations have caused researchers to question whether the original TPB decomposition hypothesis, which assumed a reaction occurring entirely in the salt solution phase, is correct. Further work is being planned to elucidate the mechanism and location of the palladium catalyzed reaction.

7.0 References

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