Sodium Tetrphenylborate Catalyst Identification: Phase B and C Statistical Design Studies

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**SODIUM TETRAPHENYLBORATE CATALYST IDENTIFICATION: PHASE B AND C
STATISTICAL DESIGN STUDIES (U)**

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1.0 Summary

Excess sodium tetraphenylborate decomposed during startup of the In-Tank Precipitation process in 1995. Several tasks, in response to this event, resulted. This work supports resolution of DNFSB Recommendation 96-1 and partially fulfills the task to identify the catalyst responsible for the decomposition. Phases B and C of the statistical design soluble sodium tetraphenylborate decomposition catalyst identification tests are complete. Observations and conclusions drawn from Phase B and C testing follow.

- All three organic species (i.e., benzene, diphenylmercury, and phenylborate intermediates) are necessary to facilitate the observed rapid decomposition of soluble sodium tetraphenylborate.
- The decomposition reaction appears zero order with respect to the organic grouping; however, their large molar ratio (with respect to palladium) prevents determining this value with any certainty.
- An increasing benzene concentration (at low concentrations) speeds the reaction (i.e., reaction not zero order with respect to benzene). However, the tests could not determine the minimum benzene concentration required to promote reaction, although a benzene concentration of 360 mg/L (i.e., the amount added in centerpoint Tests 61 and 62) does produce near-maximum rate constants.
- Palladium is the noble metal species responsible for the observed rapid decomposition. Rhodium, ruthenium, and silver proved inactive.
- A limited number of centerpoint tests suggested a reaction order less than unity with respect to palladium.
- A slow but statistically significant reaction (average $k' = 2.4 \pm 1.0 \text{ E-4 h}^{-1}$) occurred in a small number of tests. This rate appears consistent with reaction due to copper catalysis.

2.0 Introduction

Excess sodium tetraphenylborate (NaTPB) decomposed during startup of the In-Tank Precipitation (ITP) process in 1995. [Ref. 1] Several tasks, in response to this event, resulted. One task seeks to identify the catalyst responsible for the decomposition. [Ref. 2] The task includes two portions: preliminary tests and statistically designed tests. Previous reports give the results of the preliminary tests. [Ref. 3, 4] These tests assessed the relative influence of reaction conditions (for example, reaction vessel, agitation, salt solution composition, and insoluble tetraphenylborate). Results from preliminary tests defined the best conditions for subsequent statistical design tests. [Ref. 3, 4]

The statistical design tests focus on identifying key NaTPB decomposition catalysts. These designed tests, evolutionary in nature, include several phases. Thirty-six chemicals comprised the list of potential catalysts. Phase A segregated potential catalysts to differentiate between types (e.g., suspect active organics, suspect active metals, copper, etc.) of species. [Ref. 5] This segregation reduced the number of tests and determined that the interaction of a select group of organic compounds (i.e., benzene, diphenylmercury, triphenylborane, diphenylborinic acid, and phenylboronic acid, previously referred to suspect active organics) with a select group of metals (i.e., rhodium, ruthenium, palladium, and silver, previously referred to as suspect active metals) as responsible for the observed catalytic decomposition. Phase A tests demonstrated that a large number of the species found in ITP waste proved catalytically insignificant (relative to the aforementioned interaction). Table 1 contains a list of all inactive species tested as well as the two suspect active groups. The concentrations listed represent values measured in samples from Tank 48H during the 1995 reaction. The inclusion of all chemical species (except oxygen) provides a "fully-loaded" simulant of the ITP waste and, thus, should mimic the ITP NaTPB reaction. We term this simulant the Enhanced Comprehensive Catalyst, or ECC. Previous studies evaluated the reaction rates for this system. [Ref. 3 - 4]

Phase A results prompted two additional sets (Phases B and C) of statistically designed tests. The Phase B design separates the five suspect active organics into three groups: benzene, phenylborate intermediates (i.e., triphenylborane, diphenylborinic acid, and phenylboronic acid), and diphenylmercury. The Phase C design separates the four suspect active metals into individual species (i.e., palladium, rhodium, ruthenium, and silver). This document describes the results of Phase B and C statistically designed tests and is the fourth report for this task [Ref. 2] designed to identify soluble NaTPB decomposition catalysts. This task, performed as part of the Defense Nuclear Facility Safety Board (DNFSB) Recommendation 96-1 Implementation Plan [Ref. 6], partially fulfills the request by High Level Waste Engineering (HLWE) and the ITP Flow Sheet Team as defined in Task Technical Request HLW-TTR-97008. [Ref. 7]

3.0 Experimental

3.1 Statistical Design

The design of Phase B tests sought to identify the specific compound(s) in the group of suspect active organics responsible for NaTPB catalytic decomposition. The tests segregated the five members of the suspect active organics into three fractions (i.e., benzene, diphenylmercury, and phenylborate intermediates). Three fractions were selected for three reasons. First, this design permitted a full factorial design with a minimal number of tests. Secondly, personnel thought that the three fractions performed distinct mechanistic functions. Third, facility personnel can exert a degree of control over selected fractions with respect to plant operation (e.g., pump operation can remove benzene from Tank 48H). Table 2 shows the Phase B statistical design. The tests add all of the additional ECC components, including the four suspect active metals, to each Phase B test at their ECC concentrations. The table uses three values (1, 0, -1) to signify inclusion of the organic species at a representative concentration, one half of the representative concentration, or absent from the test, respectively. This statistical design examines all primary, secondary, and tertiary interactions. Phase B consists of eight statistically designed tests and two centerpoint tests.

The Phase C test design allows identification of the specific compound(s) in the group of suspect active metals responsible for NaTPB catalytic decomposition. The design segregated the suspect active metals group into individual components (i.e., ruthenium, rhodium, palladium, and silver). Table 3 shows the statistical design. This partial factorial design permits only identification of primary interactions. Since secondary and tertiary interactions between the metals seem unlikely, unlike with the suspect active organics, a fractional design is adequate. The tests add all of the additional ECC components, including the five suspect active organics, to each Phase C test at their ECC concentrations. The table uses three values (1, 0, -1) to signify inclusion of the metal species at a representative concentration, one half of the representative concentration, or absent from the test, respectively. Phase C consists of eight statistically designed tests and two centerpoint tests.

3.2 Reaction Conditions

Tests used non-radioactive simulants. Solutions were prepared from reagent grade chemicals by weighing on calibrated balances. The accuracy of glassware used to measure volumes was verified by gravimetric methods using water as a standard. [Ref. 8] Temperature measurements used thermometers calibrated by the SRTC Standards Laboratory. Temperature monitoring occurred at least once per day. The temperature targeted ± 3 °C of the stated set point. All additional measuring and test equipment used in this task received calibration or verification for accuracy prior to use.

As noted above, Table 1 lists the concentration of ECC components. Tables 2 and 3 provide a list of the statistical designs (i.e., which tests include which groups of potential catalysts or factors). Typically, tests were monitored over two weeks. Based upon conclusions drawn from preliminary test results (Ref. 3 and 4), all tests occurred in sealed 160-mL glass serum bottles at 55 °C with a nitrogen atmosphere. Each test used 2.7 M Na⁺, 48 g/L KTPB slurry containing only soluble NaTPB (i.e., no NaTPB solids). Each bottle

was charged with 100 mL of the simulant slurry (see Table 4) followed by a prescribed amount of each of the ECC components. The soluble metal species came from stock solutions prepared from common salts. For the insoluble solids, the tests used simulated Purex sludge that did not contain noble metals, copper, silver, or mercury. All tests requiring simulated sludge and MST added hydrated species. The soluble organic species (i.e., triphenylborane (3PB), diphenylborinic acid (2PB), phenylboronic acid (1PB), phenol, isopropanol, and methanol) came from an alkaline stock solution. Monosodium titanate (MST), benzene, diphenylmercury, and biphenyl were added as pure compounds. After adding all potential catalysts, each vessel was sealed.

In all tests, an initial (obtained immediately after sealing each vessel) filtrate sample was analyzed by High Performance Liquid Chromatography (HPLC) to obtain starting concentrations of NaTPB, 3PB, and 2PB. No analyses for benzene, 1PB, phenol, or soluble boron analysis occurred. Furthermore, only TPB⁻, triphenylborane, and diphenylborinic acid species were monitored in subsequent samples. Filtrate was obtained for analysis by using syringe filter discs with a 0.45 μ nominal pore size to remove solids from the slurry sample. Periodic analysis of the reaction mixtures occurred during the remainder of the testing. Slurry sampling occurred after aggressive, manual shaking for approximately 15 seconds. HPLC analysis of the filtrate from these samples allowed determination of the rate and extent of reaction. The tetraphenylborate ion (TPB⁻) reaction rate represents the TPB⁻ loss per unit time.

4.0 Results and Discussion

Tables 5 through 24 contain concentration data for NaTPB, 3PB, and 2PB for Tests 53 through 72, respectively. Sections 4.1 through 4.4 discuss the significance of the data.

4.1 Reaction Rates and Rate Constants

Reaction rates for Tests 53 through 72 were calculated based only on measured soluble NaTPB concentrations from samples taken throughout the reaction period (Equation 1). The calculations used Microsoft® Excel 5.0 for data regression analysis. Kinetic calculations yielded pseudo first-order rate constants for each reaction. Changes in the concentrations of soluble decomposition products (i.e., 3PB and 2PB) during the two weeks of testing verify that differences ($\pm 10\%$) in NaTPB concentration reflect either decomposition or error in analysis. Since decomposition of NaTPB results in the production of 3PB and eventually 2PB, these measurements provide a confirmation of NaTPB decomposition (i.e., 3PB and 2PB measurements help determine if an observed change or observed variability in NaTPB reflects decomposition or analytical error). Table 25 lists pseudo first-order rate constants for Tests 53 through 72. Sections 4.2 through 4.4 provide analysis and discussion of the data.

$$\text{Rate} = -d[\text{NaTPB}]/dt = k[\text{TPB}^-][\text{catalyst}]^n = k'[\text{TPB}^-], \text{ where } k' = k[\text{catalyst}]^n \quad (1)$$

4.2 Phase B Statistical Analysis

The following summary table lists rate constants for those tests investigating the influence of various organic compounds. Rate constants marked as NRD (i.e., no reaction detected) indicate statistically insignificant changes in NaTPB concentration and limited 3PB and 2PB concentrations. Statistical analysis of the data indicates that a tertiary interaction of the three organic species (i.e., benzene, diphenylmercury, and phenylborate intermediates) promotes the reaction with the suspect active metals. The statistical analysis indicates no primary or secondary effects. In simpler terms, the tests indicate the presence of all three organic groups at the same time accelerates the reaction but no individual group causes an increase in the observed rate. Only tests containing all three resulted in statistically significant rapid reaction rates.

Figure 1 provides further evidence of the tertiary dependence by comparing the [NaTPB] of Tests 56, 58, 59, and 60. Test 60, containing all three organic species, shows the fastest reaction (i.e., greatest loss of NaTPB). Test 58 is the next most reactive system. Test 58 started without adding benzene. The data suggest that the decomposition reaction accelerated after producing benzene from decomposition of a

Test #	Pseudo-First Order Rate Constant, k ($\text{h}^{-1} \times 10^4$) ^a	Phenylborate Intermediates ^b	Benzene ^c	Diphenylmercury ^c
53	NRD	-1	-1	-1
54	NRD	-1	-1	1
55	NRD	-1	1	-1
56	11.7 $\pm$ 7.7 (overall) 0.7 (early in test) 22.3 (end of test)	-1	1	1
57	NRD	1	-1	-1
58	41.2 $\pm$ 15.2 (overall) 5.6 (early in test) 35.2 (middle of test) 88.1 (end of test)	1	-1	1
59	0.8 $\pm$ 0.7	1	1	-1
60	93.0 $\pm$ 25.4	1	1	1
61	97.7 $\pm$ 13.9	0	0	0
62	85.2 $\pm$ 7.8	0	0	0

^aObtained from equation, $\text{Rate} = -d[\text{NaTPB}]/dt = k[\text{TPB}][\text{Catalyst}]^n = k'[\text{TPB}]$, where $k' = k[\text{Catalyst}]^n$

^bNRD represents "no reaction detected" and indicates [TPB] data variance not statistically significant at a 95% confidence level. 3PB and 2PB data verifies the lack of reaction.

^c-1 indicates the group absent from the test, 1 indicates the group present in the test at concentrations listed in Table 1, and 0 indicates the group present with concentrations one half of those listed in Table 1.

portion of the phenylborate intermediates or copper catalyzed NaTPB decomposition. Rate constants obtained from the three different times during testing (i.e., early, middle, and end) successively increase as shown in the following table. This pattern suggests that increasing benzene concentration speeds the reaction (i.e., reaction not zero order with respect to benzene). However, the data does not allow one to estimate the minimum benzene concentration required to promote reaction although a benzene concentration of 360 mg/L (i.e., the amount added in Tests 61 and 62) does produce near-maximum rate constants.

A similar hypothesis appears valid for Test 56 which lacked phenylborate intermediates at the start of the test. Similarly, the small amount of NaTPB decomposition (due to copper decomposition) might have generated the required organic species and the catalytic reaction began. The limited data does not permit determining the required concentration of intermediates. In terms of order of reaction, one expects that benzene would form in Test 58 faster than phenylborate intermediates in Test 56. Test 58, without added benzene, contains both intermediates and their decomposition catalysts at the onset. Benzene formed from these decompositions from the start of testing at a fairly rapid rate. In Test 56 without added intermediates, decomposition of NaTPB provided the only source of the necessary intermediates. To produce the intermediates, a much slower (relative to the observed rapid NaTPB decomposition) copper catalyzed NaTPB decomposition mechanism occurs. Therefore, Test 58 should start reacting earlier than Test 56. Test 59 cannot produce diphenylmercury in-situ (i.e., no other sources of mercury exist in the tests). Therefore, Test 59 cannot react via a mechanism influenced by mercury compounds. Figure 1 indicates a slow reaction rate for Test 59 suggesting diphenylmercury (or perhaps a form of mercury) participates as a necessary factor for the observed rapid catalytic reaction. Interestingly, a slow but statistically significant reaction ($k' = (0.8 \pm 0.7) \text{ E-4 h}^{-1}$) occurred in Test 59. This rate appears consistent with reaction due to copper catalysis. Previous work suggests a rate constant of 1.7 E-4 h^{-1} for copper catalysis under these test conditions. [Ref. 9]

Figure 1. Demonstration of the reactivity of tests containing all three organic species (Test 60) and two of the three organic species (Tests 56, 58, and 59).

The lack of a rapid reaction (i.e., a k' approximately two orders of magnitude greater than observed) in Test 59 differs with data from several other reaction tests without mercury which showed a significant reaction. [Ref. 3,10, 11] The cause for this discrepancy remains unknown. The author could not identify any single parameter that differed among these tests. Several, but not all, of these tests occurred in larger systems. Difference in physical properties may occur due to changes in scale. For example, the diffusion of benzene or oxygen in the system scales with depth of the solution; larger systems will experience different concentrations of these species. Catalyst preparation also differed among the tests. The tests described in this report used a slightly different simulated sludge from that used in the large scale tests. These laboratory scale tests which exhibited a dependence on mercury used simulated Purex sludge prepared without noble metals (i.e., palladium, ruthenium, rhodium, and silver) or copper. These tests added palladium, ruthenium, rhodium, silver, and copper individually (palladium, ruthenium, rhodium, and silver were added from acidic stock solutions). The mercury-free, large scale tests used simulated Purex sludge containing copper and palladium, ruthenium, rhodium, and silver. Analysis of the sludge materials continues as does comparison of the tests to examine the discrepancy.

4.3 Phase C Statistical Analysis

The following summary table lists rate constants for those tests investigating the influence of various metals. Rate constants marked as NRD (i.e., no reaction detected) indicate statistically insignificant changes in 3PB and 2PB concentrations. Statistical analysis of the data indicates that palladium exhibits a primary effect on the reaction. The other three metals did not exhibit any effect. The statistical design did not permit identifying secondary or tertiary interactions. Figure 2 clearly shows the influence of palladium. Without palladium, only a very slow or non-detectable reaction proceeds. Similar to Test 59, a slow reaction occurred in Tests 63 and 65 ($k' = (3.2 \pm 2.9) \text{ E-4 h}^{-1}$ and $(3.1 \pm 2.7) \text{ E-4 h}^{-1}$, respectively). Again these rates most likely reflect copper catalysis.

Test #	Pseudo First Order Rate Constant, k' ($\text{h}^{-1} \times 10^4$) ^a	Rhodium ^b	Ruthenium ^b	Palladium ^b	Silver ^b
63	3.2 ± 2.9	-1	-1	-1	-1
64	134.6 ± 29.1	-1	-1	1	1
65	3.1 ± 2.7	-1	1	-1	1
66	105.5 ± 37.0	-1	1	1	-1
67	NRD	1	-1	-1	1
68	131.5 ± 43.0	1	-1	1	-1
69	NRD	1	1	-1	-1
70	98.0 ± 16.1	1	1	1	1
71	96.6 ± 30.4	0	0	0	0
72	95.0 ± 33.8	0	0	0	0

^aObtained from equation, $\text{Rate} = -d[\text{NaTPB}]/dt = k[\text{TPB}][\text{Catalyst}]^n = k'[\text{TPB}]$, where $k' = k[\text{Catalyst}]^n$

^bNRD represents "no reaction detected" and indicates [TPB] data variance not statistically significant at a 95% confidence level. 3PB and 2PB data verifies the lack of reaction.

^c-1 indicates the group absent from the test, 1 indicates the group present in the test at concentrations listed in Table 1, and 0 indicates the group present with concentrations one half of those listed in Table 1.

Figure 2. Demonstration of the reactivity of tests containing palladium.

4.4 Reaction Order

Testing demonstrated that palladium, benzene, phenylborate intermediates, and diphenylmercury play integral parts in the catalytic system for the observed rapid decomposition of NaTPB. The author further analyzed Phase B and Phase C data to determine the reaction order of each reactant. The limited amount of data for tests with varying concentrations of each component prevents determining the reaction order with high certainty. The data indicate a reaction order for palladium of less than unity. The reaction appears zero order with respect to the three organic groups. However, the increasing rate constant observed for Test 58 indicates a non-zero reaction order with respect to benzene. The table below presents the molar ratio (relative to palladium) of each of the components at their respective ECC concentration. Given the large molar ratio for the organic species, one would not expect to discern the reaction order with such a limited data set.

Component	Concentration (mg/L)	Concentration (10^{-5} moles/L)	Molar Ratio (relative to palladium)
Palladium	2.6	2.4	1.0
Benzene	720	920	380
Diphenylmercury	150	42	18
3PB	125	52	22
2PB	125	69	29
1PB	125	100	42
Copper	1.7	2.7	1.1

5.0 Conclusions

The second and third sets, Phases B and C, of statistical design catalyst identification tests are complete. Phase B testing determined the presence of all three organic species (i.e., benzene, diphenylmercury, and phenylborate intermediates) as necessary to facilitate the observed rapid decomposition. Removal of any one of the three species either delays or prevents reaction. Phase C testing identified palladium as the influential metal in catalyzing the decomposition at the high rates of these experiments. (Copper, in comparable concentrations at these condition, only contributes to ~1% of the measured reaction rates.) The limited number of centerpoint tests indicate a reaction order of less than unity with respect to palladium. The reaction appears zero order with respect to the organics; however, their large molar ratio (with respect to palladium) prevents determining this dependency with any certainty from these tests.

6.0 Path Forward

The final set (i.e., Phase D) of these statistically designed tests investigates the potential catalytic activity of two conditions or chemicals omitted from all previous catalyst identification testing. These experiments will examine the effect of radiolysis and the potential catalytic effect of uranium under conditions similar to those discussed in this document. Additionally, further work may prove necessary to understand the discrepancies observed with respect to diphenylmercury.

7.0 Tables

Table 1. Enhanced Comprehensive Catalyst components for Phase B and C statistical design catalyst identification tests with target concentrations provided in parentheses.

Inactive Components

methanol (5 mg/L)
isopropanol (50 mg/L)
phenol (125 mg/L)
biphenyl (150 mg/L)
copper (1.7 mg/L)
cadmium (0.4 mg/L)
molybdenum (12 mg/L)
cerium (0.3 mg/L)
silicon (16 mg/L)
selenium (1 mg/L)
arsenic (0.04 mg/L)
tin (2.1 mg/L)
cobalt (0.04 mg/L)
calcium (12.2 mg/L)
strontium (0.1 mg/L)
lanthanum (0.05 mg/L)
iron (579 mg/L)
chromium (64 mg/L)
zinc (12.8 mg/L)
manganese (118 mg/L)
nickel (50 mg/L)
aluminum (96 mg/L)
magnesium (2 mg/L)
zirconium (50 mg/L)
lead (6 mg/L)
monosodium titanate (2 g/L)

Suspect Active Organics

benzene (720 mg/L)
diphenylmercury (150 mg/L)
Phenylborate intermediates
• 3PB (125 mg/L)
• 2PB (125 mg/L)
• 1PB (125 mg/L)

Suspect Active Metals

ruthenium (5.4 mg/L)
rhodium (1.4 mg/L)
palladium (2.6 mg/L)
silver (6.8 mg/L)

Table 2: Phase B statistical design for suspect active organics identification testing.

Test #	Phenylborate Intermediates ^a	Benzene ^a	Diphenyl-mercury ^a
53	-1	-1	-1
54	-1	-1	1
55	-1	1	-1
56	-1	1	1
57	1	-1	-1
58	1	-1	1
59	1	1	-1
60	1	1	1
61	0	0	0
62	0	0	0

^a -1 indicates the group absent from the test. 1 indicates the group present with concentrations listed in Table 1. 0 indicates the group present with concentrations one half of those listed in Table 1.

Table 3: Phase C statistical design for suspect active metals identification testing.

Test #	Rhodium ^a	Ruthenium ^a	Palladium ^a	Silver ^a
63	-1	-1	-1	-1
64	-1	-1	1	1
65	-1	1	-1	1
66	-1	1	1	-1
67	1	-1	-1	1
68	1	-1	1	-1
69	1	1	-1	-1
70	1	1	1	1
71	0	0	0	0
72	0	0	0	0

^a -1 indicates the group absent from the test. 1 indicates the group present with concentrations listed in Table 1. 0 indicates the group present with concentrations one half of those listed in Table 1.

Table 4. Standard tetraphenylborate slurry simulant for Phase A statistical design catalyst identification tests (target concentrations).

Component	2.7 M Na ⁺ Slurry Concentration
sodium ^a	2.66 M
hydroxide	1.49 M
nitrite	0.39 M
nitrate	0.38 M
aluminate	0.09 M
sulfate	0.006 M
carbonate	0.10 M
chloride	0.008 M
fluoride	0.004 M
phosphate	0.003 M
TPB ^(b)	0.02 M
NaTPB (insoluble) ^b	0 g/L
KTPB (insoluble) ^c	48 g/L

^aTheoretical (determined by filtrate density). [Ref. 11]

^bTheoretical (determined by sodium ion concentration). [Ref. 12]

^cConcentration represents ~ 4 wt % KTPB.

Table 5. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 53.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	10054	< 10	< 10
15.2	9318	< 10	< 10
59.1	8767	< 10	< 10
153	9415	< 10	< 10
321	8380	< 10	< 10

Table 6. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 54.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9866	< 10	< 10
15.2	9654	< 10	< 10
59.1	8944	< 10	< 10
153	9585	< 10	< 10
321	8860	< 10	< 10

Table 7. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 55.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	10006	< 10	< 10
15.2	9823	< 10	< 10
59.1	8548	< 10	< 10
153	9978	< 10	< 10
321	8777	< 10	< 10

Table 8. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 56.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	10033	< 10	< 10
15.2	9863	< 10	< 10
59.1	9021	< 10	< 10
153	10099	16	< 10
321	9165	31	< 10
650	4389	1871	744

Table 9. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 57.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9884	86	125
15.2	9306	86	122
59.1	8727	69	69
153	9385	84	36
321	8424	76	< 10

Table 10. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 58.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9956	87	156
15.2	9260	82	130
59.1	8983	91	78
153	8902	545	75
321	4927	2377	367
486	2247	2880	845
650	527	2357	1071

Table 11. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 59.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	10003	86	157
15.2	9769	83	118
59.1	9320	80	62
153	10010	86	39
321	8976	80	< 10
486	9578	88	< 10
650	8490	84	< 10
817	8960	78	< 10
982	9243	57	5
1149	8751	54	< 10
1317	8774	69	< 10

Table 12. Soluble sodium tetraphenylborate, triphenylborane (3PB), diphenylborinic acid (2PB), and potassium concentrations versus time for Test 60.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	Soluble Potassium (mg/L) ^a
0.0	9976	87	116	NA
15.2	9635	256	139	NA
59.1	6125	2047	481	NA
153	3252	3165	1679	NA
321	577	2323	2217	NA
486	26	1107	1885	3.445
817	10	66	322	40.300
1149	< 10	5	81	79.850

^aNA indicates no analysis performed.

Table 13. Soluble sodium tetraphenylborate, triphenylborane (3PB), diphenylborinic acid (2PB), and potassium concentrations versus time for Test 61.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	Soluble Potassium (mg/L) ^a
0.0	9694	42	44	NA
15.2	9588	59	61	NA
59.1	7431	1224	297	NA
153	3848	2783	1524	NA
321	749	1989	1550	NA
486	54	1034	1065	< 0.160
817	5	66	202	33.020
1149	< 10	7	52	52.950

^aNA indicates no analysis performed.

Table 14. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 62.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9965	44	79
15.2	9760	85	70
59.1	6120	1751	538
153	3336	2670	1728
321	806	2272	1350
486	154	1464	1500

Table 15. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 63.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9846	86	151
15.2	9735	80	118
59.1	9190	95	68
153	9095	96	43
321	8800	75	< 10

Table 16. Soluble sodium tetraphenylborate, triphenylborane (3PB), diphenylborinic acid (2PB), and potassium concentrations versus time for Test 64.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	Soluble Potassium (mg/L) ^a
0.0	9903	77	153	NA
15.2	7828	1037	449	NA
59.1	4440	2265	1038	NA
153	1994	2594	1516	NA
321	287	1845	1811	NA
486	< 10	587	1293	12.920
817	< 10	38	248	43.940
1149	< 10	4	78	76.550

^aNA indicates no analysis performed.

Table 17. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 65.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9801	84	153
15.2	9692	80	116
59.1	9235	79	84
153	9011	102	24
321	8828	77	< 10

Table 18. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 66.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9991	84	158
15.2	9522	195	140
59.1	5927	1773	714
153	3461	2475	1246
321	1019	1861	1402
486	40	733	1401

Table 19. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 67.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9355	79	148
15.2	10043	90	121
59.1	9238	78	60
153	9036	79	25
321	8860	74	< 10

Table 20. Soluble sodium tetraphenylborate, triphenylborane (3PB), diphenylborinic acid (2PB), and potassium concentrations versus time for Test 68.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)	Soluble Potassium (mg/L) ^a
0.0	9930	88	158	NA
15.2	8208	904	458	NA
59.1	4790	2173	1045	NA
153	2495	2150	1573	NA
321	490	1430	1541	NA
486	< 10	476	1135	21.420
817	< 10	16	187	95.030
1149	< 10	< 10	59	170.750

^aNA indicates no analysis performed.

Table 21. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 69.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9885	82	152
15.2	9692	80	116
59.1	9161	95	65
153	9104	77	34
321	9131	75	< 10

Table 22. Soluble sodium tetraphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 70.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9738	82	155
15.2	9410	284	144
59.1	5385	2196	674
153	2944	2572	1193
321	667	2174	1670
486	72	1233	1516

Table 23. Soluble sodium tetrphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 71.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	9743	95	141
15.2	9705	108	122
59.1	7830	908	177
153	4468	2463	711
321	1500	2383	1300
486	308	1742	1690
650	< 10	545	1044

Table 24. Soluble sodium tetrphenylborate, triphenylborane (3PB) and diphenylborinic acid (2PB) concentrations versus time for Test 72.

Reaction Time (h)	Soluble NaTPB (mg/L)	3PB (mg/L)	2PB (mg/L)
0.0	10294	87	162
15.2	9594	120	123
59.1	7503	1283	227
153	4713	2485	675
321	1684	2787	1796
486	394	2023	2128
650	< 10	916	1811

Table 25. Kinetics data for Phase B and C statistical design catalyst identification Tests 53 through 72.

Test	Pseudo first Order Rate Constant ^a , k' (h ⁻¹ * 1 E-4)	Comments ^b
53	3.9 ± 6.6	no reaction detected
54	2.4 ± 5.1	no reaction detected
55	2.6 ± 9.4	no reaction detected
56	11.7 ± 7.7	
57	3.4 ± 6.1	no reaction detected
58	41.2 ± 15.2	
59	0.8 ± 0.7	
60	93.0 ± 25.4	
61	97.7 ± 13.9	
62	85.2 ± 7.8	
63	3.2 ± 2.9	
64	134.6 ± 29.1	
65	3.1 ± 2.7	
66	105.5 ± 37.0	
67	2.7 ± 4.4	no reaction detected
68	131.5 ± 43.0	
69	2.1 ± 3.8	no reaction detected
70	98.0 ± 16.1	
71	96.6 ± 30.4	
72	95.0 ± 33.8	

^aObtained from equation, Rate = -d[NaTPB]/dt = k[TPB][Catalyst]ⁿ = k'[TPB], where k' = k[Catalyst]ⁿ

^b"No reaction detected" indicates [TPB] data not statistically significant at a 95% confidence level. 3PB and 2PB data verifies the lack of a significant reaction.

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