Low Temperature Decomposition Rates for Tetraphenylborate Ion

by

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DOE Contract No. **DE-AC09-96SR18500**

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WSRC-TR-98-00342, Rev. 0

Keywords: In-Tank Process, Benzene
Retention: Permanent

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Publication Date: October 2, 1998

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LOW TEMPERATURE DECOMPOSITION RATES FOR TETRAPHENYLBORATE ION

By D. D. WALKER

SUMMARY

Palladium catalyzes the decomposition of tetraphenylborate in alkaline solutions. Researchers postulate that the decomposition mechanism includes a catalyst activation step and a tetraphenylborate (TPB^-) decomposition step. Experiments reported below separated the two steps and clarified the mechanism of the reaction. These tests show the following.

- Tetraphenylborate reacts at a measurable rate at 25 °C in the presence of active catalyst.
  - The activation energy for the reaction is 46.8 (±3.4) kJ/mole.
  - No "temperature cliff" exists between 35 °C and 25 °C below which TPB^- does not decompose.

- Catalyst activation is very sensitive to oxygen.
  - Oxygen prevents catalyst activation at 25 °C in laboratory-scale tests.
  - In the absence of oxygen, the catalyst activation step causes a delay in the onset of TPB^- decomposition. The length of the delay depends on temperature, lasting less than a day at 55 °C and over a week at 25 °C for laboratory-scale tests.
  - In the absence of oxygen, the catalyst activation step depends on the initial concentration of Pd(II).

- The rate of decomposition of TPB^- at 45 °C varied only 30% when the initial Pd (II) concentration varied over the range 0.65 to 5.2 mg Pd/L.

- No reaction occurred at 45 °C when platinum(IV) replaced palladium(II).
  - The platinum(IV) did not convert to an insoluble form as does palladium when activated.

INTRODUCTION

Previous studies indicated that palladium is catalyzes rapid decomposition of alkaline tetraphenylborate slurries.[1-5] Additional evidence suggests that Pd(II) reduces to Pd(0) during catalyst activation.[6] Further use of tetraphenylborate ion in the decontamination of radioactive waste may require removal of the catalyst or cooling to temperatures at which the decomposition reaction proceeds slowly and does not adversely affect processing.

Recent tests[7] showed that tetraphenylborate did not react appreciably at 25 °C over six months suggesting the potential to avoid the decomposition at low temperatures. The lack of reaction at low temperature could reflect very slow kinetics at the lower temperature, or may indicate a catalyst "deactivation" process. Previous tests in the temperature range 35 to 70 °C provided a low precision estimate of the activation energy of the reaction with which to predict the rate of reaction at 25 °C. To understand the observations at 25 °C, experiments must separate the catalyst activation step and the subsequent reaction with TPB^-. Tests described in this report represent an initial attempt to separate the two steps and determine the rate and activation energy of the reaction between active catalyst and TPB^-. The results of these tests indicate that the absence of reaction at 25 °C was caused by failure to activate the catalyst or the presence of a deactivating mechanism. In the presence of activated catalyst, the decomposition reaction rate is significant.

This work fulfills a request from P. L. Rutland, "TPB Solids Stability," Technical Task Request #HLE-TAR-98059, Rev.0, March 11, 1998. The work complies with the following plan: D. D. Walker, "Scoping Tests for Low Temperature Tetraphenylborate Decomposition," SRT-LWP-98-0019, Rev.0, June 5, 1998. The testing supports design of the Small Tank Precipitation process.[8]

TEST DESIGN AND RESULTS

Researchers initially investigated the rate of reaction of TPB^- following catalyst activation at temperatures in the range 25 to 55 °C, the rate of reaction of TPB^- without catalyst activation over the same temperature range, and the effect of initial Pd concentration on the rate of TPB^- decomposition at 45 °C. After the reaction of TPB^- at 25 °C occurred, a comparison of the previous tests by Barnes[7] and the current tests revealed several potentially significant differences. Additional tests examined several of these differences.

All of the tests slurries contained 5 wt % KTPB solids in a 2.8 molar Na^+ salt solution with an anion distribution reflecting the average SRS soluble waste composition (Table A-1, Appendix A). The slurries were carefully prepared to contain soluble TPB^- (approximately 0.015 molar) but no sodium tetraphenylborate (NaTPB) solids. The presence of solids would provide an additional source of TPB^- and result in concentration changes that do not follow simple reaction kinetics. The low sodium concentration ensured sufficient soluble TPB^- initially present to allow catalyst activation and subsequent monitoring of the decomposition reaction. The tests used catalyst components added at the same concentrations as previous tests[1-5] (called the Extended Comprehensive Catalyst, or 1X ECC). Table A-2, Appendix A, lists the catalyst components and concentrations.

TPB^- Reaction Rates with Activated Catalyst

These tests activated catalyst by heating at 55 °C for approximately 19 hours. Within this time, approximately half of the initial soluble tetraphenylborate decomposed. The

slurries then cooled to the desired temperature (25, 30, 35, or 45 °C). Subsequent sampling and analysis provided data for calculation of the reaction rates at the lower temperatures. In all cases, the reaction rates showed first order dependence on the TPB^- concentration.

Reaction rate (molar/hr) = k $[TPB^-]$

where k = rate constant (h^{-1})
and $[TPB^-]$ = concentration of TPB^- (molar)

The rate constants equal the slope of a plot of time versus the logarithm of the TPB^- concentration. Figure 1 shows the change in TPB^- concentration with time. Appendix contains tables of the concentration data. Table I, below, lists the rate constants for loss of TPB^- ion. Figure 2 shows an Arrhenius plot of the rate constants. The data is linear and the triplicate data points at 25 °C do not suggest any unusual temperature dependence in the 25 to 35 °C range. The slope of the line yields the activation energy of the reaction based on the following equation.

$$\ln k = -E_a/RT$$

where E_a is the Arrhenius activation energy (kJ/mole)
R is the gas constant (8.314 J/°K/mole)
and T is temperature (°K).

The activation energy is 46.8 (±3.4) kJ/mole. The magnitude of the activation energy indicates the reaction rate will double for every 10 °C increase in temperature in the range 25 to 55 °C. This result is within the range of previously reported values, but with a much smaller uncertainty. Crawford[9] and Peterson[10] previously estimated the activation energy, respectively, as 43±20 and 39±20 kJ/mole.

Table I. Rate Constants (k) for Reaction of TPB^- with Activated Catalyst*

Temperature (°C)	k (h^{-1})
25	-.00452 ± .00017
30	-.00511
35	-.00709
45	-.0124
55	-.0273

* Catalyst activated by heating the slurry to 55 °C for 19 hours. Calculations of rate constants use only data collected after 19 hours.

FIGURE 1. Changes in Tetraphenylborate Concentration

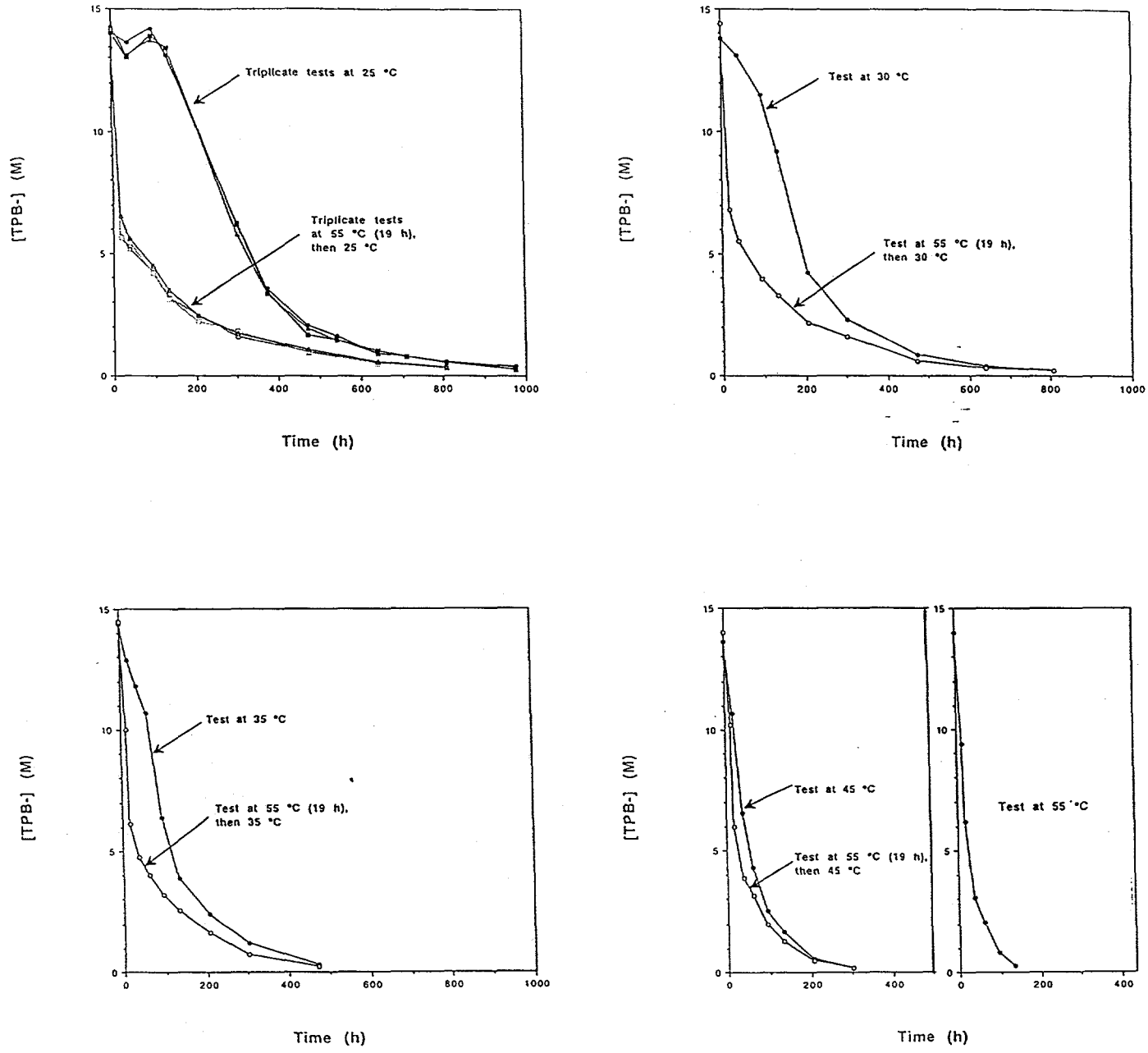
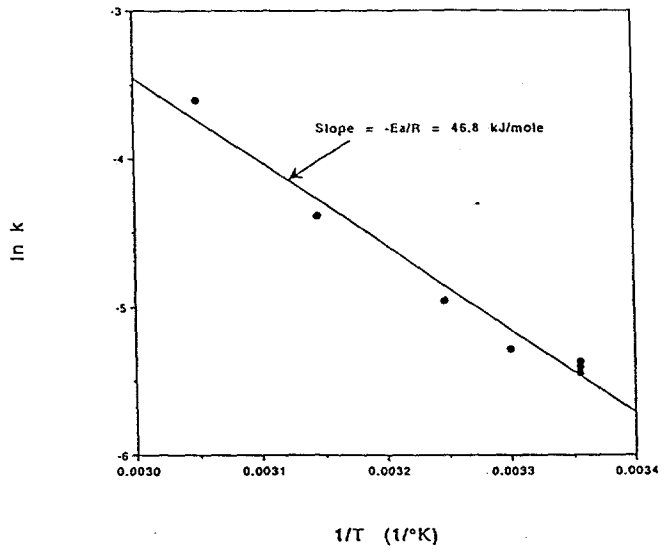


Figure 2. Temperature Dependence of the Rate of Reaction of TPB^- with Activated Catalyst.



Tests without Catalyst Activation at 55 °C

A second set of tests placed the slurries in water baths at the lower temperatures at the start of the test. Table II lists the rate constants from these experiments. Figure 1 shows the changes in TPB^- concentration for these tests. At each temperature, the reaction was slow initially but eventually showed first order dependence on the concentration of TPB^-. The time required to reach the maximum rate decreased as the temperature increased. The author calculated the rate constants for the first order reaction from data after the inflection point in each graph. The rate constants averaged 12% higher than in the corresponding test with the catalyst activated by heating to 55 °C for 19 hours. The difference could reflect more complete activation over the longer time periods in spite of the lower temperatures.

TABLE II. Rate Constants (k) for Reaction of TPB^- without Preactivation of Catalyst

Temperature (°C)	k (h^{-1})*
25	-.00476 ± .00004
30	-.00529
35	-.00874
45	-.0145

*Rate constants were calculated from data following the inflection point in the graph of [TPB^-] vs. time (see Figure 1).

TABLE III. Effect of Temperature and Palladium Concentration on Delay Times

Temperature (°C)	Delay time (h)
25	200
25, 5X Pd*	<24
30	100
35	70
45	20

*Pd concentration (13 mg/L) five times greater than the nominal ECC concentration (2.6 mg/L) used in other tests.

The length of the delay in the onset of the rapid reaction varied with temperature and Pd concentration. Table III lists approximate delay times estimated from the inflection point in the graphs. At all temperatures above 25 °C, measurable loss of TPB^- (~25%) occurred during the delay period. At 25 °C, loss of TPB^- was not significant for the 200 hours prior to onset of the reaction.

Effect of Palladium Concentration

Testing measured the effect of the initial palladium concentration at 25 and 45 °C. Figure 3 shows the changes in [TPB^-] for each test and Table IV lists the rate constants. The Pd dependence observed in these tests appears contradictory. At 25 °C, the rate constant varies approximately proportional to the initial Pd concentration. However, at 45 °C, the rate constant appears relatively independent of the initial palladium concentration, varying by only 50% as the Pd changed by 800%. The results suggest either of two possible explanations. The reaction mechanism may shift between 25 and 45 °C such that Pd participates in the rate-determining step at the lower, but not at the higher, temperature. Alternatively, the catalyst activation reaction at 25 °C may depend on the amount of Pd while the yield at higher temperature does not. Either explanation seems to suggest a much more complex reaction system than seems probable. Hence, the dependency of reaction rate on palladium requires additional investigation.

Effect of Oxygen

The decomposition within two weeks at 25 °C in the tests without catalyst activation by treatment at 55 °C contrasts with previous work in which negligible reaction occurred for over six months. Comparison of the two test protocols identified the following differences.

1. Although both test sets used the same palladium stock solution, unidentified solids precipitated between the two studies. The solids might contain Pd(0), the presumed form of the activated catalyst. Use of this solution could have provided Pd in the correct oxidation, thus circumventing the activation step. The soluble palladium concentration did not change significantly due to the precipitation of solids.

FIGURE 3. Effect of Initial Palladium Concentration on Decomposition of TPB^-

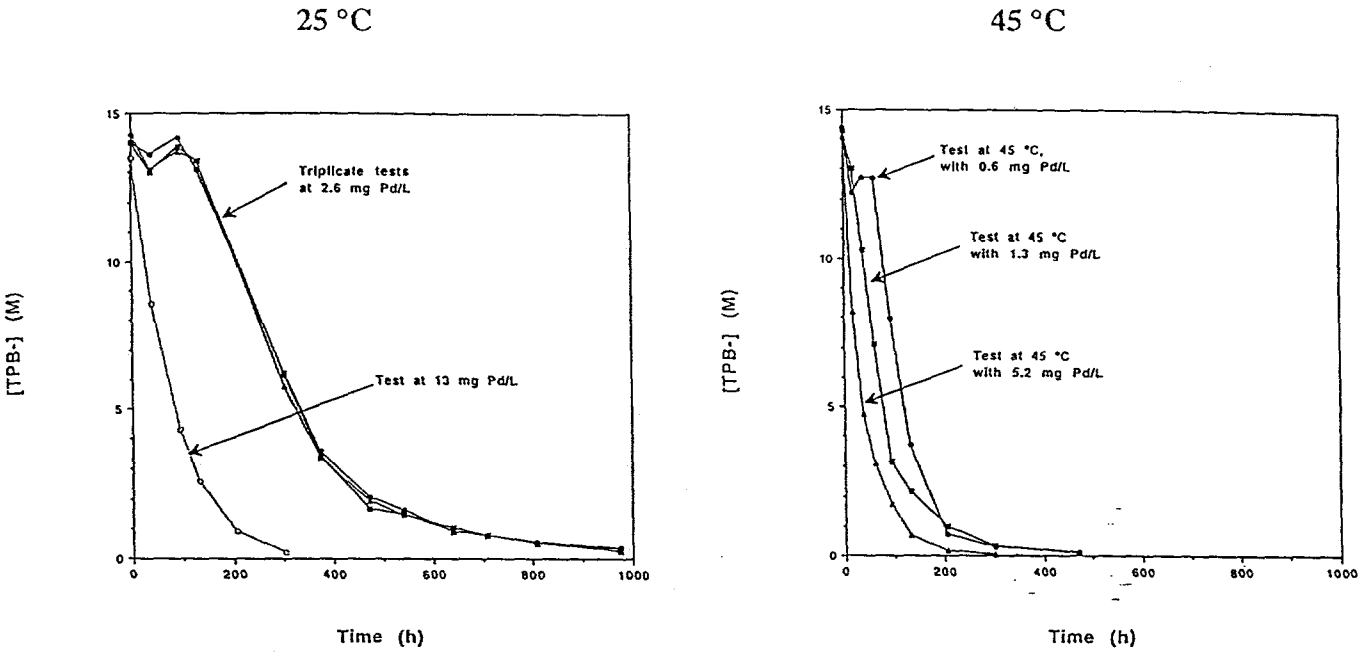


TABLE IV. Effect of Initial Palladium Concentration on Rate Constants (k)*

Temperature (°C)	Initial Pd (mg/L)	k (h^{-1})
25	2.6	-0.00452(±.00017)
	13.	-0.0141
45	0.65	-0.0162
	1.3	-0.0125
	2.6	-0.0145
	5.2	-0.0184

* From isothermal tests without catalyst activation at 55 °C.

2. The tests by Barnes used significantly higher concentrations of the intermediate compounds triphenylborane (3PB), diphenylborinic acid (2PB), and phenylboronic acid (1PB). Previous studies suggest that higher concentrations of the intermediates can prevent reaction of TPB^-.
3. The tests by Barnes used a covered water bath, thus excluding light except during sampling. The current tests used clear serum vials under laboratory fluorescent lighting. Light might initiate reaction.
4. The tests by Barnes were initially purged, but subsequent sampling likely allowed air to leak into the serum vials. The current tests excluded air by pressurizing the vials with nitrogen during sampling. Previous studies showed that oxygen affects the reaction. In particular, oxygen can prevent reduction of Pd(II) to Pd(0), the likely form of the active catalyst.

Additional tests examined if any of the differences contributed to the observed reactivity difference between the two test sets. Table V lists the test conditions and results. The results indicate the presence of oxygen as the likely reason for the lack of reaction in the Barnes tests. However, the presence of high intermediates also affects the reaction. The high intermediate concentrations appear to reduce the reactivity but the effect seems too small to cause the difference observed in the two test sets. Barnes' tests could detect a 23% drop in TPB^- and corresponding increase in 3PB and 2PB such as seen in the "high intermediates" test in Table V.

TABLE V. Test Conditions and Results *

Test Condition	TPB^- Loss after 426 h (%)
Control*	82
Pd solids in stock solution removed by 0.2 micron filter	79
High intermediates (increased by 400% to match Barnes' concentrations)	23
Light eliminated by painting vial black	81
Air injected at each sampling time	No reaction (<6%)
Combined (used filtered stock solution, high intermediates, blackened vial, and injected air)	No reaction (<3%)

* The control test repeated the protocol described in Appendix A. All tests used 2.7 M Na^+ salt solution at 25 °C with 1X ECC (2.6 mg Pd/L) unless otherwise indicated.

Effect of Platinum

Platinum is a potential substitute for palladium based on their chemical similarity. Previous work with Pd(0) on titania particles showed it catalyzed the decomposition of tetraphenylborate.[11] The effectiveness of platinum as a catalyst in simulated SRS waste was tested by substituting soluble Pt(IV) for palladium in the ECC catalyst system. However, no reaction occurred in over 800 hours at 45 °C and the platinum concentration in solution did not decrease during the 800 hour test. The lack of reaction may indicate a slow activation step rather than lack of catalytic activity.

DISCUSSION

These test results show that the palladium catalyst can activate at 25 °C in the absence of oxygen and that tetraphenylborate reacts at a measurable rate at 25 °C. No "temperature cliff" exists between 35 °C and 25 °C below which TPB^- does not decompose. The rate of decomposition is first order in TPB^- concentration, so the rate changes as the reaction proceeds. The results of the study allow calculation of the rate of loss of TPB^- at 25 °C from the rate constants and the TPB^- concentration. This information allows prediction of the amount of excess tetraphenylborate required to maintain low cesium concentrations in the presence of the catalytic reaction. Estimated rates of benzene generation can be calculated with additional assumptions about the stoichiometry of the reaction and the rate of decomposition of the intermediates. Future work should extract rates of decomposition of 3PB and 2PB from the data in the appendix of this report.

The sensitivity of the reaction to the presence of oxygen suggests the potential to prevent decomposition (or more likely, catalyst activation) by maintaining some concentration of oxygen in the slurry. The amount of oxygen required and the method of maintaining the minimum concentration require further study.

UNCERTAINTIES IN CURRENT WORK

The results of the recent tests suggest that further investigation in the following areas for would increase our understanding of the decomposition of tetraphenylborate.

- Effect of oxygen on catalyst activation and decomposition of TPB^-.
  The results of the current tests suggest the presence of oxygen prevents catalyst activation. Additional testing to confirm this and measure the amount of oxygen required to prevent activation could lead to methods for preventing the decomposition reaction.

- Effect of Palladium concentration on reaction rate.
  The lack of a rate dependence on the initial Pd concentration at 45 °C deserves further investigation. Additional tests should monitor the change in soluble Pd

and attempt to characterize the insoluble Pd produced during the reaction. This information would help understand the design requirements and process value of using palladium removal to prevent the catalyzed decomposition of tetraphenylborate.

- Reactivity of platinum.

  The lack of reactivity of platinum contradicts other reports. The discrepancy may result from differences in the from of the Pt used. Resolution of this discrepancy requires additional testing. Understanding the relative reactivity of the two metals may prove necessary to interpretation of previous tests with radioactive waste.[12]

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APPENDIX A
Experimental

Preparation of Slurries

Researchers prepared simulated KTPB slurries (nominally 5 wt % KTPB solids) with the composition shown in Table A-1. The critical feature of these slurries was the presence of excess soluble tetraphenylborate (~15 mM TPB^-) but no solid NaTPB. Researchers added ~0.8 M NaTPB solution to a ~0.15 M KNO_3 solution to ensure complete and rapid precipitation of KTPB, followed by addition of soluble sodium salts to achieve 2.8 M Na^+. At this point, the slurry was analyzed to verify the presence of soluble tetraphenylborate at the expected concentration based on material balance. All chemicals were reagent grade. NaTPB (99+% purity) came from Aldrich Chemical Company. Next, portions of slurry (125 mL) were placed in glass serum vials (nominal 160 mL internal volume). The components of the catalyst system (Table B-2) except benzene were added. Several of the tests varied particular components of the catalyst. The vials were capped and purged with nitrogen gas to remove air. In two cases, the vials were purged with air . Finally, the benzene was added via syringe and the vials shaken to mix the benzene. A 15-mL portion of slurry was removed from each vial (initial samples). The vials were then placed in temperature controlled water baths. The vials were maintained at temperature, sealed, and unstirred for the duration of the test. The bath temperature was automatically controlled to ±0.2 °C and was checked daily with a mercury-in-glass thermometer. Periodically, the vials were removed from the baths, shaken briefly by hand, and sampled by syringe. During sampling, the vials were pressurized with nitrogen to prevent air in-leakage. The vials were out of the baths less than three minutes for each sampling.

TABLE A-1 Composition of Simulated Waste Slurry (Excluding Catalyst Components)*

Component	Concentration (molar)
Na^+	2.8
NO_3^-	1.07
NO_2^-	0.39
OH^-	0.85
AlO_2^-	0.17
CO_3^{2-}	0.078
SO_4^{2-}	0.073
Cl^-	0.013
F^-	0.008
PO_4^{3-}	0.00
TPB^-	0.0015
KTPB	60 g/L (~5 wt %)

*See Table A-2 for catalyst components.

TABLE A-2. Catalyst Components in Simulant Slurries

Insoluble Components (wt % of slurry)
1.2 g/L (~1 wt %) sludge
1.2 g/L (~1 wt %) monosodium titanate

Sludge composition (wt % of dry sludge)

Al	4.8	Cu	0.1
Fe	18.8	Mg	0.1
Mn	5.9	Ni	2.5
Ru	0.23	Pb	0.3
Rh	0.06	Zn	0.2
Cr	0.2	Zr	2.5

Metal Additives (mg/L)

Ca(II)	12.2	Ru(III)	0.8	Cd(II)	0.4
Sr(II)	0.1	Co(II)	0.04	Hg(II)	2.2
La(III)	0.05	Rh(III)	0.2	Si(IV)	16
Ce(IV)	0.3	Sn(III)	2.1	Cr(VI)	60
Cu(II)	1.7	Pb(II)	1.2	Mo(VI)	12.
Ag(I)	0.6	As(IV)	0.04	Fe(III)	2.6
Zn(II)	8.8	Se(VI)	1		

Organic Additives (mg/L)

3PB	500	Diphenylmercury	150
2PB	250	Methanol	4
Phenol	250	Isopropanol	40
Benzene	750		

Analytical Results

The samples were analyzed for organic compounds (NaTPB, 3PB, 2PB, 1PB, and phenol) and potassium ion (following loss of all soluble NaTPB). Table A-3 lists the analytical results from the initial tests and Table A-4 lists results from the followup tests.

Analytical Methods

Analytical Development Section of SRTC performed the following analyses .

Phenylboronic acid (1PB) and phenol measurements used high performance liquid chromatography (HPLC) on a Hewlett Packard LC with a 2.1x250 mm Dychrom Chemosorb 5-ODS-UH column using acetonitrile-water eluent. Tetraphenylborate, triphenylboron (3PB), and diphenylborinic acid (2PB) measurements used the same model instrument and column with a 0.1% ammonium phosphate buffered acetonitrile-methanol-water eluent (La-mar-ka, Inc., Baton Rouge, LA). The HPLC instrument methods are described in Manual L16.1, Procedure #ADS-2655. The methodology of sample preparation, standards, and standard preparation for HPLC analyses is described

consistent performance of the HPLC method. The control samples contained NaTPB, 1PB and phenol. The results for the controls agreed consistently within ±10% of the average.

Potassium ion concentrations of aqueous samples used flame atomic absorption with a Varian SpectrAA-400 spectrometer. The samples were first digested in nitric acid by microwave heating. Each digested sample was diluted 1:4(sample:suppressant) in a suppressant solution of 2000 µg/mL cesium. For more concentrated samples, additional dilutions were made with 1600 µg/mL cesium. The method is described in Manual L16.1, Procedure #ADS-1549.

Soluble palladium and platinum concentrations were measured by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) using a VG Elemental PQ2 instrument. Samples were diluted and acidified to a pH < 2 using dilute nitric acid. The method is described in Manual L16.1, Procedure #ADS-1553.

TABLE A-3. Analytical Results for Low Temperature Tests

Temp		25 deg C				55 deg (19 h), 25 deg C. (remainder)							
Catalyst		Control, no catalyst				Control, no catalyst							
Date	Elapsed Time (h)	TPB- (mM)	3PB (mM)	2PB (mM)		TPB- (mM)	3PB (mM)	2PB (mM)					
14-Jul	0.0	14.2	0.97	0.68		13.5	0.94	0.69					
15-Jul	18.7					12	0.84	0.74					
16-Jul	38.0	13.7	0.94	0.73		13.4	0.92	0.65					
18-Jul	94.4	14.2	0.95	0.64		13.7	0.95	0.65					
20-Jul	134.7	14.5	0.98	0.7		13.4	0.96	0.68					
27-Jul	302.0	14.9	0.99	0.75		14.9	1	0.78					
3-Aug	470.7	14.3	0.97	0.79		14.4	0.97	0.77					
10-Aug	638.7	14.4	0.96	0.74		13	0.9	0.7					
17-Aug	807.6	15.0	1.00	0.72		14.6	1	0.86					
24-Aug	975.4	14.8	0.99	0.73		14.1	0.97	0.73					
Temp			25 deg C				25 deg C				25 deg C		
Catalyst			1X Pd				1X Pd				1X Pd		
Date	Elapsed Time (h)	TPB- (mM)	3PB (mM)	2PB (mM)		TPB- (mM)	3PB (mM)	2PB (mM)		TPB- (mM)	3PB (mM)	2PB (mM)	
14-Jul	0.0	14.0	0.98	0.68		14.0	0.97	0.68		14.3	1.00	0.70	
16-Jul	38.0	13.6	1.00	0.68		13.0	0.97	0.66		13.1	1.01	0.69	
18-Jul	94.4	14.2	1.66	0.73		13.9	1.60	0.71		13.7	1.63	0.75	
20-Jul	134.7	13.1	2.50	0.75		13.4	2.54	0.74		13.4	2.73	0.79	
27-Jul	302.0	6.24	9.95	2.35		6.16	10.1	2.39		5.78	10.2	2.47	
30-Jul	373.6	3.58	12.0	3.20		3.44	12.0	3.22		3.38	12.3	3.33	
3-Aug	470.7	2.05	12.7	4.43		1.69	11.1	3.68		1.94	12.9	4.50	
6-Aug	541.0	1.63	13.8	5.13		1.47	13.9	5.08		1.48	14.2	5.36	
10-Aug	638.7	0.90	10.9	4.44		1.02	12.8	4.97		0.91	12.6	5.04	
13-Aug	710.0	0.79	12.9	5.65		0.77	13.4	5.38		0.79	13.4	5.53	
17-Aug	807.6	0.56	12.8	6.39		0.52	13.0	6.01		0.50	12.8	6.12	
24-Aug	975.4	0.37	11.1	6.81		0.27	11.6	6.53		0.34	11.8	6.94	
Temp	55 deg C (19 h), 25 deg C (remainder)					55 deg C (19 h), 25 deg C (remainder)				55 deg C (19 h), 25 deg C (remainder)			
Catalyst		1X Pd					1X Pd				1X Pd		
Date	Elapsed Time (h)	TPB- (mM)	3PB (mM)	2PB (mM)		TPB- (mM)	3PB (mM)	2PB (mM)		TPB- (mM)	3PB (mM)	2PB (mM)	
14-Jul	0.0	13.4	0.50	1.25		13.8	0.95	0.68		14.2	0.98	0.69	
15-Jul	18.7	5.71	7.57	2.05		5.65	7.53	1.96		6.55	8.09	2.13	
16-Jul	38.0	5.17	8.33	2.36		5.42	8.43	2.38		5.61	8.07	2.14	
18-Jul	94.4	4.23	10.8	3.20		4.19	10.7	3.09		4.50	10.3	3.01	
20-Jul	134.7	3.17	11.5	3.54		3.13	11.3	3.48		3.49	11.0	3.51	
23-Jul	205.7	2.46	12.3	4.19		2.21	12.2	4.28		2.45	11.8	4.20	
27-Jul	302.0	1.59	12.3	4.63		1.79	12.7	4.86		1.74	12.1	4.68	
3-Aug	470.7	1.00	11.8	5.30		0.95	12.2	5.67		1.08	12.0	5.38	
10-Aug	638.7	0.53	11.6	6.01		0.47	11.5	6.08		0.58	11.9	6.14	
17-Aug	807.6	0.31	11.8	7.31		0.30	11.6	7.28		0.35	11.8	7.25	
Temp		25 deg C					30 deg C			55 deg C (19 h), 30 deg C (remainder)			
Catalyst		5X Pd					1X Pd				1X Pd		
Date	Elapsed Time (h)	TPB- (mM)	3PB (mM)	2PB (mM)		TPB- (mM)	3PB (mM)	2PB (mM)		TPB- (mM)	3PB (mM)	2PB (mM)	
14-Jul	0.0	13.5	0.95	0.70		13.8	0.98	0.68		14.4	0.99	0.69	
15-Jul	18.7									6.79	7.83	1.92	
16-Jul	38.0	8.56	6.57	1.18		13.1	1.21	0.71		5.53	8.15	2.11	
18-Jul	94.4	4.33	11.8	2.50		11.5	3.66	0.79		3.97	10.9	3.22	
20-Jul	134.7	2.57	13.8	3.36		9.18	7.02	1.35		3.28	11.4	3.62	
23-Jul	205.7	0.90	14.3	4.61		4.23	11.2	2.99		2.14	11.8	4.25	
27-Jul	302.0	0.21	12.1	6.47		2.27	12.5	4.14		1.59	11.9	5.02	
3-Aug	470.7					0.86	12.2	5.54		0.61	11.3	6.18	
10-Aug	638.7					0.38	11.5	6.87		0.31	10.8	7.55	
17-Aug	807.6					0.22	10.3	8.31		0.21	10.0	9.32	

TABLE A-3. Analytical Results for Low Temperature Tests (continued)

Temp		35 deg C			55 deg C (19 h), 35 deg C (remainder)								
Catalyst		1X Pd					1X Pd						
Date	Elapsed Time (h)	TPB- (mM)	3PB (mM)	2PB (mM)		TPB- (mM)	3PB (mM)	2PB (mM)					
14-Jul	0.0	14.4	0.98	0.75		14.5	0.99	0.69					
15-Jul	13.1					10.0	5.67	1.02					
15-Jul	18.7					6.14	7.50	1.64					
15-Jul	19.0	12.9	1.19	0.66									
16-Jul	38.0	11.8	2.66	0.64		4.76	8.63	2.35					
17-Jul	62.7	10.7	6.31	1.16		4.00	10.7	3.31					
18-Jul	94.4	6.37	9.45	2.01		3.19	11.4	3.72					
20-Jul	134.7	3.89	12.8	3.23		2.56	12.4	4.28					
23-Jul	205.7	2.40	12.6	4.19		1.64	12.7	5.16					
27-Jul	302.0	1.20	12.7	5.14		0.74	12.1	6.10					
3-Aug	470.7	0.30	11.4	7.23		0.23	10.5	8.28					

Temp		45 deg C			55 deg C (19 h), 45 deg C (remainder)								
Catalyst		1X Pd					1X Pd						
Date	Elapsed Time (h)	TPB- (mM)	3PB (mM)	2PB (mM)		TPB- (mM)	3PB (mM)	2PB (mM)					
14-Jul	0.0	13.6	0.95	0.74		14.0	0.96	0.66					
15-Jul	13.1					10.2	5.77	1.05					
15-Jul	18.7					6.01	7.26	1.64					
15-Jul	19.0	10.7	3.01	0.73									
16-Jul	38.0	6.54	7.29	1.46		3.87	9.20	2.84					
17-Jul	62.7	4.32	11.0	3.29		3.14	11.2	3.88					
18-Jul	94.4	2.54	11.3	3.93		1.99	11.0	4.29					
20-Jul	134.7	1.67	12.8	5.33		1.31	12.1	5.68					
23-Jul	205.7	0.55	11.7	7.34		0.49	11.2	8.09					
27-Jul	302.0	0.16	9.33	9.79		0.17	8.45	9.99					

Temp		55 deg C				45 deg C							
Catalyst		1X Pd				Pt catalyst							
Date	Elapsed Time (h)	TPB- (mM)	3PB (mM)	2PB (mM)		TPB- (mM)	3PB (mM)	2PB (mM)	Pt (mg/L)				
14-Jul	0.0	14.0	0.97	0.68		14.3	1.00	0.69	2.5				
15-Jul	13.1	9.38	6.07	1.21									
15-Jul	18.7	6.19	8.03	2.12									
15-Jul	19.0					12.1	0.84	0.57					
16-Jul	38.0	3.05	9.28	3.16		12.7	0.88	0.62	2.4				
17-Jul	62.7	2.08	11.6	4.92		14.1	0.98	0.45					
18-Jul	94.4	0.84	10.8	6.60		13.7	0.96	0.40					
20-Jul	134.7	0.28	9.61	9.41		14.4	1.00	0.34	2.4				
27-Jul	302.0					13.5	1.36	0.14					
3-Aug	470.7					13.1	1.49	0.09					
10-Aug	638.7					13.4	1.50	0.15					
17-Aug	807.6					13.4	1.53	0.82					
24-Aug	975.4					11.4	1.38	0.93					

Temp		45 deg C				45 deg C				45 deg C		
Catalyst		25% Pd				50% Pd				2X Pd		
Date	Elapsed Time (h)	TPB- (mM)	3PB (mM)	2PB (mM)		TPB- (mM)	3PB (mM)	2PB (mM)		TPB- (mM)	3PB (mM)	2PB (mM)
14-Jul	0.0	14.4	0.99	0.72		14.3	1.00	0.71		14.1	1	0.73
15-Jul	19.0	12.2	0.94	0.60		13.0	1.18	0.64		8.21	6.78	1.24
16-Jul	39.0	12.7	1.14	0.59		10.3	3.62	0.73		4.74	9.54	2.3
17-Jul	62.7	12.7	3.39	0.60		7.10	8.67	1.85		3.1	11.5	3.43
18-Jul	94.4	7.97	7.90	1.46		3.14	10.7	3.86		1.73	12.2	4.72
20-Jul	134.7	3.69	11.2	3.55		2.14	12.1	4.91		0.67	12.5	6.99
23-Jul	205.7	0.73	10.7	6.41		0.98	12.1	6.25		0.18		10.1
27-Jul	302.0	0.31	10.2	7.31		0.35	10.3	7.46		0.05	5.39	12.2
3-Aug	470.7	0.11	8.51	9.59		0.10	7.26	10.3				

TABLE A-4. Analytical Results from Followup Low Temperature Tests

Temp			25 deg C				25 deg C	
			Control			Pd test (filtered)		
Date	Elapsed	TPB-	3PB	2PB		NaTPB	3PB	2PB
	Time (h)	(mM)	(mM)	(mM)		(mM)	(mM)	(mM)
4-Sep	0.0	12.9	0.92	0.66		12.4	0.91	0.65
10-Sep	140.3	11.7	2.28	0.86		12.6	1.76	0.67
16-Sep	283.4	6.52	7.95	1.80		8.23	0.65	1.47
22-Sep	426.5	2.28	11.4	3.59		2.66	11.0	3.23
Temp			25 deg C				25 deg C	
		High Intermediates					No light	
Date	Elapsed	TPB-	3PB	2PB		NaTPB	3PB	2PB
	Time (h)	(mM)	(mM)	(mM)		(mM)	(mM)	(mM)
4-Sep	0.0	12.7	3.50	2.45		13.1	0.95	0.64
10-Sep	140.3	12.7	3.57	2.31		11.8	1.67	0.68
16-Sep	283.4	10.4	4.90	2.03		7.98	6.74	1.46
22-Sep	426.5	9.76	6.81	2.75		2.53	11.1	3.25
Temp			25 deg C				25 deg C	
			Air purged				Combined	
Date	Elapsed	TPB-	3PB	2PB		NaTPB	3PB	2PB
	Time (h)	(mM)	(mM)	(mM)		(mM)	(mM)	(mM)
4-Sep	0.0	13.2	0.94	0.64		12.8	3.69	2.52
10-Sep	140.3	13.0	0.97	0.61		13.0	3.66	2.13
16-Sep	283.4	13.1	1.25	0.64		13.0	3.62	2.04
22-Sep	426.5	12.4	1.43	0.60		13.5	3.71	1.66

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