Effects of Oxygen and Catalyst on Tetraphenylborate Decomposition Rate

by

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EFFECTS OF OXYGEN AND CATALYST ON TETRAPHENYLBORATE DECOMPOSITION RATE

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EFFECTS OF OXYGEN AND CATALYST ON TETRAPHENYLBORATE DECOMPOSITION RATE

By D. D. WALKER

SUMMARY

Previous studies indicate that palladium catalyzes rapid decomposition of alkaline tetraphenylborate slurries.¹⁻⁴ Oxygen inhibits the reaction at low temperature (25 °C), presumably by preventing activation of the catalyst. The present study investigated oxygen's inhibiting effectiveness at higher temperature (45 °C) and catalyst concentrations. Additional tests investigated the effect of metals (Pd or Pt) and form (soluble, or supported on BaSO₄ or carbon) on the rate of reaction with soluble TPB⁻. The following statements summarize the test results.

- Aeration using oxygen gas does not provide a robust method for preventing the decomposition of soluble TPB⁻.
 - Although oxygen prevented decomposition at 25 °C and 2.6 mg Pd/L, it did not significantly inhibit the decomposition at 45 °C and 5.2 mg Pd/L (double the nominal catalyst concentration).
- Despite many chemical similarities between platinum and palladium, neither soluble Pt(IV) nor Pt(0) supported on activated carbon catalyze the decomposition of tetraphenylborate ion.
- The support for the Pd catalyst affects the reaction rate.
 - Pd(0) supported on activated carbon reacts at approximately half the rate of Pd(0) supported on BaSO₄.

INTRODUCTION

Palladium catalyzes the decomposition of tetraphenylborate in alkaline solutions.¹ Previous research suggests Pd(0) is the active form of the catalyst.²⁻⁴ At 25 °C with oxygen present, the decomposition reaction of tetraphenylborate ion (TPB⁻) initiates slowly or not at all. The results are consistent with a mechanism in which oxygen prevents the reduction of Pd(II) to Pd(0), thus inhibiting the catalyzed decomposition of TPB⁻. Depending on the effectiveness of oxygen in preventing catalyst activation, it might prove feasible to prevent decomposition of tetraphenylborate. Thus, researchers conducted an experiment at higher temperature (45 °C) and palladium concentration (5.2 mg/L). A tetraphenylborate slurry was stirred in the presence of oxygen to counteract the activation of the catalyst. Additional tests investigated the catalytic activity of platinum and the effect of the catalyst support. Previous reports conflicted on the catalytic activity

of platinum. Researchers at Pacific Northwest National Laboratory⁵ (PNNL) found platinum supported on TiO₂, ZrO₂, or activated carbon caused degradation of tetraphenylborate at 25 °C and neutral pH. Researchers at the Savannah River Site found no degradation of TPB⁻ in the presence of Pt(IV) under alkaline conditions.³ This study included a test using platinum supported by activated carbon to investigate this discrepancy. In addition, testing investigated the effect of the support material (BaSO₄ and activated carbon) on the reactivity of palladium.

This work fulfills a request from P. L. Rutland, "TPB Solids Stability," Technical Task Request #HLE-TTR-98039, Rev. 0, March 11, 1998. The work complies with the following plan: D. D. Walker, "Technical Task Plan for Solids Stability Studies of Tetraphenylborate Slurries - Additional Studies," WSRC-RP-98-00055, Rev.0, March 4, 1998.

TEST DESIGN AND RESULTS

Tests investigated the effect of oxygen on the reaction rate, and the effect of catalyst metal and substrate on catalyst activity. Table I provides a summary of the test conditions. Appendix A describes experimental details of the tests.

Oxygen Test

Previous test results indicated oxygen inhibits the palladium-catalyzed decomposition of soluble tetraphenylborate in alkaline solutions.²⁻⁴ At 25 °C and 2.6 mg Pd/L of slurry, no

TABLE I. Summary Test Conditions

<u>Condition</u>	<u>Oxygen Test</u>	<u>Catalyst Test</u>
Temperature	45 °C	45 °C
Na ⁺	2.8 M	2.8 M
KTPB solids concentration	60 g/L (~5 wt %)	60 g/L (~5 wt %)
Sludge solids	4.8 g/L (~0.4 wt %)	2.4 g/L (~0.2 wt %)
Noble metal (Pd or Pt)	Pd(II) solution, 5.2 mg/L	Pd or Pt, 2.6 mg/L in various forms
Other ECC components*	Double nominal	Nominal
Atmosphere	purged with O ₂ or N ₂	sealed under N ₂
Mixing	continuous	no mixing
Vessels	glass	glass

* ECC = Enhanced Comprehensive Catalyst. See Appendix A and Reference 5 for composition.

Figure 1. Loss of Tetraphenylborate Under Oxygen or Nitrogen Atmosphere (45 °C).

reaction occurred. However, at 45 °C and 13 mg Pd/L of slurry, the reaction proceeded in unstirred, sealed containers. Under these conditions (unstirred and sealed), local concentrations of oxygen may decrease sufficiently to allow catalyst activation. The current study explored the slurry reactivity under conditions more favorable for catalyst activation (i.e., at higher temperature and higher palladium concentration) to determine if an oxygen atmosphere can prevent catalyst activation. The test design included a simultaneous control test under nitrogen.

Both the nitrogen- and oxygen-purged slurries reacted at 45 °C. Figure 1 shows the decrease in soluble tetraphenylborate concentration during the test. Changes in the triphenylboron (3PB) and diphenylborinic acid (2PB) concentrations also confirm the loss of tetraphenylborate due to decomposition (Appendix A, Table A-4). As obvious from the figure, at elevated temperatures and these palladium concentrations, controlling the oxygen in the atmosphere above the slurry did not significantly slow the reaction.

Catalyst Test

The work also investigated the importance of the metal (Pd or Pt) and the form (soluble, or supported on BaSO₄ or activated carbon). Platinum is a potential catalytic substitute for palladium based on their chemical similarity. In a single previous test at 45 °C, soluble platinum(IV) did not catalyze the decomposition of tetraphenylborate, presumably because it did not reduce to Pt(0).³ Researchers postulated that they could observe Pt catalysis if the experimental conditions avoided the apparently slow reduction step by starting with a reduced form of Pt (i.e., Pt(0) on a solid support). Thus, we repeated the

test with soluble Pt(IV) and compared to a test using Pt(0) on activated carbon (abbreviated as Pt[C]). Another test examined the effect of the supporting phase for the Pd(0). Pd(0) supported on BaSO₄ (abbreviated as Pd[BaSO₄]) catalyzed the tetraphenylborate decomposition at a slightly slower rate than soluble Pd(IV). Since Pd[BaSO₄] proves relatively inactive compared to Pd[C] in many systems, researchers postulated that Pd[C] might serve as a more effective catalyst for the tetraphenylborate decomposition. We tested this hypothesis by comparing the reaction of Pd[BaSO₄] to Pd[C].

Neither of the two Pt catalysts reacted (Figure 2). A slight decrease in the TPB⁻ concentration appears at the last sampling point (451 hours), but neither 3PB (Figure 3) nor 2PB (Figure 4) concentrations show a corresponding increase. The apparent decrease probably results from random analytical or sampling error. The lack of reactivity with platinum removes a possible explanation for the reactivity observed in radioactive waste tests.⁷ In those earlier tests, personnel suggested high reactivity of a small amount of Pt as a possible explanation for discrepancies between real waste (which may contain small amounts of Pt) and the ECC simulant (which lacks Pt).

With Pd(0), the substrate appears to slightly influence the decomposition rate. Figure 2 shows that both Pd[BaSO₄] and Pd[C] reacted. The observed rate of decomposition with Pd[BaSO₄] proved approximately twice as rapid as with Pd[C]. Table II lists initial rates of tetraphenylborate decomposition from experiments using different Pd catalyst forms. Soluble Pd(II), however, provides a much faster reaction (see Table 2). The differences in reactivity may reflect differences in particle size or dispersion of the Pd(0).

DISCUSSION

The results of the oxygen atmosphere test indicate that stirring in the presence of oxygen gas does not provide a robust method for preventing the decomposition of soluble TPB⁻. Although oxygen prevented decomposition at 25 °C and 2.6 mg Pd/L, it did not significantly inhibit the decomposition at 45 °C and 5.2 mg Pd/L (i.e., double the nominal catalyst concentration). Because of its limitations, this approach appears impractical for successful process application. The diffusion path length for oxygen in process equipment likely significantly exceeds that in the laboratory scale equipment. Hence, oxygenation to inhibit TPB⁻ decomposition will prove less effective than demonstrated in these tests. Oxygenation by sparging (i.e., direct injection of oxygen into the slurry) would prove ineffective because foaming will limit the sparging rate. Use of oxygen gas or air also raises flammability concerns that argue against this approach.

Despite many chemical similarities between platinum and palladium, neither soluble Pt(IV) nor Pt(0) supported on activated carbon catalyzed the decomposition of tetraphenylborate ion in simulated alkaline waste. Unpublished results from researchers at PNNL indicate platinum will catalyze TPB⁻ decomposition in neutral solution.⁵ The difference in pH between the two sets of tests likely causes the observed difference in reactivity. Platinum is not a fission product and only trace amounts -- much less than

Figure 2. Effect of Catalyst on the Decomposition of Tetraphenylborate.

Figure 3. Effect of Catalyst on the Concentration of 3PB (45 deg.C)

Figure 4. Effect of Catalyst on the Concentration of 2PB (45 deg C).

TABLE II. Comparison of Pd Catalyst Reaction Rates

<u>Catalyst form</u>	<u>Rate of loss of TPB⁻</u> <u>(mM/day)</u>	<u>[Pd]</u> <u>(mg/L)</u>	<u>Temperature</u> <u>(°C)</u>	<u>Reference</u>
soluble Pd(II)	0.6	11	25	2
Pd[BaSO ₄]	0.3	11	25	2
Pd[BaSO ₄]	0.25*	5.2	45	This report.
Pd[C]	0.11*	5.2	45	This report.

*Rates calculated from the slope of graphs in Figure 2.

palladium ~~z~~ exist in Savannah River Site radioactive waste. The low potential concentrations and lack of reactivity of platinum eliminates a possible explanation for the reactivity observed in radioactive waste tests.⁷ Previously, personnel speculated high specific reactivity of Pt as a possible explanation for discrepancies between reaction rates in SRS radioactive waste and the ECC simulant (which lacks Pt).

The test results indicate the substrate supporting the Pd catalyst affects the reaction rate. However, the variance appears relatively small (less than a factor of x2) between two very different supports (BaSO₄ and activated carbon). Both of the supported catalysts prove less reactive (per mg of Pd) than systems starting with soluble Pt(IV), suggesting that the Pd(0) acts as the most effective catalyst when present as free Pd(0) particles or deposited directly on KTPB particles.

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APPENDIX A

Experimental

Preparation of Slurries

Researchers prepared a simulated KTPB slurry (nominally 5 wt % KTPB solids) with the composition shown in Table A-1. Researchers added ~0.8 M NaTPB solution to a ~0.15 M KNO₃ solution to ensure complete and rapid precipitation of KTPB, then added the soluble sodium salts to achieve 2.8 M Na⁺. All chemicals were reagent grade. NaTPB (99+% purity) came from Aldrich Chemical Company.

Oxygen vs. Nitrogen Atmosphere Test

The apparatus for this test included glass reaction vessels (9.0 cm diam x 10 cm tall) fitted with gas inlet and outlets (Figure A-1). House supply lines provided nitrogen or oxygen gas to purge the vapor space of the vessels. Low flow metering valves controlled the flow of gas. To preclude evaporation of the KTPB slurries, the gas streams were saturated with water using gas bubblers filled with deionized water. A water bath at 45.0±0.2 °C provided temperature control for the bubblers and reaction vessels. Researchers weighed tetraphenylborate slurry (131 g, 115 mL), sludge (3.18 g of 16.6 wt % solids slurry), and monosodium titanate (3.42 g of 14.5 wt % solids slurry) into each vessel. Magnetic stir bars agitated the slurry as purge gas (5 mL/min) flushed the vapor space. Bubbling the purge gas into the slurry was avoided because the slurry forms a persistent foam. The ECC metal and organic components (Table A-2) and soluble Pd(II) (5.2 mg Pd/L) were then added to the slurries via syringe through septum-covered sampling ports in the tops of the vessels. Periodically, samples (~5 mL) were removed via syringe, filtered using disposable acrylic copolymer syringe filters (0.45 micron nominal pore size, Gelman Sciences), and the filtrate analyzed for tetraphenylborate ion, triphenylboron, and diphenylborinic acid.

Catalyst Test

Researchers weighed slurry (141 g, 125 mL), sludge (1.83 g of 16.6 wt % solids slurry), and monosodium titanate (1.84 g of 14.5 wt % solids slurry) into glass beakers. The remaining ECC metal and organic components (Table A-2) except benzene were added via syringe to the stirred slurry. To each portion of slurry was added one of the catalyst forms (Table A-3). Enough of the catalyst form was added to achieve 11 mg Pd or Pt per liter of slurry. After stirring for one hour, approximately 130 mL of slurry were placed in 150-mL glass serum bottles. Researchers capped the serum bottles with Teflon-lined serum caps, purged the vials with nitrogen, added the benzene (Table A-2), and placed the vials in the water bath at 45 °C. The remaining slurry in the beaker was used for the initial (zero time) sample. The vials were maintained at temperature, sealed, and unstirred for the duration of the test. Periodically, the vials were removed from the water

FIGURE A-1. Experimental Apparatus for Oxygen Atmosphere Test

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

<u>Component</u>	<u>Concentration (molar)</u>
Na ⁺	2.8
OH ⁻	0.84
NO ₃ ⁻	1.06
NO ₂ ⁻	0.39
AlO ₂ ⁻	0.17
CO ₃ ²⁻	0.08
SO ₄ ²⁻	0.07
Cl ⁻	0.013
F ⁻	0.008
PO ₄ ³⁻	0.005
TPB ⁻	0.002
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)

2.4 g/L (~0.2 wt %) sludge

2.4 g/L (~0.2 wt %) monosodium titanate

Sludge composition (wt % of dry sludge):

Al	4.8	Cu	0.1
Fe	28.8	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	125	Diphenylmercury	150
2PB	125	Methanol	5
1PB	125	Isopropanol	50
Benzene	720	Phenol	125
Biphenyl	150		

* The amounts listed are nominal ECC catalyst concentrations (Ref.6). The oxygen atmosphere test used twice these concentrations. Pd (a component of the complete ECC catalyst system) is not listed because it was a variable in the tests. The nominal Pd concentration is 2.6 mg/L.

TABLE A-3. Catalyst Forms and Sources

<u>Form</u>	<u>Source</u>	<u>Vendor</u>
Pd[BaSO ₄]	5 wt % reduced Pd on powdered BaSO ₄	Alfa Aesar
Pd[C]	3 wt % on activated carbon, 50 wt % water slurry	Alfa Aesar
Pt(IV) solution	Pt(IV) chloride in 0.1 M HCl	High Purity Standards
Pt[C]	3 wt % on activated carbon, 50wt % water slurry	Alfa Aesar

bath, shaken briefly by hand, and sampled by syringe. During sampling, the vials were pressurized with nitrogen to prevent oxygen in-leakage.

Analytical Results

The samples were analyzed for tetraphenylborate ion, triphenylboron, and diphenylborinic acid. Table A-4 lists the analytical results.

Analytical Methods

The following analyses were performed by the Analytical Development Section of SRTC.

Tetraphenylborate, triphenylboron (3PB), and diphenylborinic acid (2PB) were measured by high performance liquid chromatography (HPLC) on a Hewlett Packard LC with a 2.1x250 mm Dychrom Chemosorb 5-ODS-UH column using a 0.1% ammonium phosphate buffered acetonitrile-methanol-water eluent (La-mar-ka, Inc., Baton Rouge, LA). Manual L16.1, Procedure #ADS-2655 describes the HPLC method. Sample and standard preparation for HPLC analyses is described in SRT-ADS-96-0438.

TABLE A-4. Analytical Results

Elapsed Time (hours)	Concentration (mM)					
	Oxygen			Nitrogen		
	NaTPB	3PB	2PB	NaTPB	3PB	2PB
0.0	12.00	1.84	1.33	12.20	1.84	1.34
18.6	10.60	2.37	1.46	9.70	4.01	1.28
40.3	6.08	4.13	2.00	4.88	8.31	2.21
111.5	2.28	3.61	5.90	0.48	6.92	7.83
186.8	0.21	0.80	8.25	0.29	3.52	8.58
280.5	<.03	0.14	6.60	0.49	3.14	5.66

	Pt(IV) solution			Pt[C]		
	NaTPB	3PB	2PB	NaTPB	3PB	2PB
0.0	9.94	0.82	0.64	9.81	0.83	0.68
21.9	10.01	0.87	0.51	10.12	1.04	0.56
117.9	9.95	0.90	0.42	9.57	1.09	0.54
186.5	9.38	0.91	0.46	9.31	1.12	0.41
291.5	10.86	1.01	0.22	10.57	1.23	--
354.0	10.98	1.07	0.31	10.72	1.27	0.46
451.5	9.90	0.95	0.26	8.82	1.07	0.37

	Pd[C]			Pd[BaSO4]		
	NaTPB	3PB	2PB	NaTPB	3PB	2PB
0.0	9.65	0.89	0.69	10.49	0.88	0.69
21.9	10.00	1.13	0.70	9.74	0.90	0.58
117.9	8.65	1.26	0.88	9.38	1.47	0.93
186.5	8.25	1.38	0.96	8.04	1.81	1.06
291.5	9.10	1.76	1.11	7.46	2.58	1.23
354.0	8.78	2.13	1.27	7.49	3.35	1.32
451.5	6.98	2.32	1.03	5.03	3.45	1.25

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