Copper-Catalyzed Decomposition at Diphenylborinic Acid and Phenylboronic Acid

by

W. R. Wilmarth

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

C. L. Crawford

R. A. Peterson

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W. R. Wilmarth
C. L. Crawford
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Westinghouse Savannah River Company
Savannah River Technology Center
Aiken, SC 29808

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W. R. Wilmarth, C. L. Crawford and R. A. Peterson
Waste Processing Technology Section
Savannah River Technology Center
Westinghouse Savannah River Company

Abstract

This report describes studies of the decomposition of diphenylborinic acid and phenylboronic acid at 25 °C and 40 °C in 1.5 M sodium hydroxide under continuous flowing air. The results of these experiments provide kinetic rate data for use in benzene formation modeling for the chemical process in the In-Tank Precipitation facilities. The results suggest pseudo-first order rate constants of $0.026 \pm 0.001 \text{ h}^{-1}$ and $0.019 \pm 0.004 \text{ h}^{-1}$ for diphenylborinic acid at 40 °C and 25 °C, respectively. For phenylboronic acid, the pseudo-first order rate constants measured $0.0385 \pm 0.003 \text{ h}^{-1}$ and $0.0094 \pm 0.003 \text{ h}^{-1}$ at 40 °C and 25 °C, respectively. However, the rate of decomposition of phenylboronic acid was observed to decrease in the presence of diphenylborinic acid. In conjunction with previous work, these results indicate activation energies of $56 \pm 21 \text{ kJ/mol}$ for the decomposition of diphenylborinic acid and $73.05 \pm 0.08 \text{ kJ/mol}$ for the decomposition of phenylboronic acid.

Introduction

The behavior of the lower phenylborates (diphenylborinic acid and phenylboronic acid) proves important to the general understanding of the chemistry in the In-Tank Precipitation (ITP) facility.¹ The decomposition of diphenylborinic acid (2PB) and phenylboronic acid (1PB) increases the benzene generation rate for the inerted portions of ITP (Tanks 48H and 49H) and may provide a major contribution to the generation rate of benzene in the air-based operations for filtrate storage (Tank 50H). Therefore, High-Level Waste Engineering requested studies of these tetraphenylborate decomposition products under simulated waste tank chemistries to ascertain rate-limiting kinetic data.²

Previously, Hyder³ studied the effect of oxygen on the decomposition of diphenylborinic acid and phenylboronic acid. The results of this work indicate that the decomposition rate increases in the presence of oxygen. Other researchers⁴⁻⁵ showed that copper appeared to provide the maximum decomposition rate for 2PB and 1PB relative to other potential transition metal, organic, or sludge-based catalysts.

This work reports the results of a decomposition study of 2PB and 1PB in a flowing air-based system with copper as the catalyst. The results at 25 °C and 40 °C along with data from Hyder and others allow one to model the temperature dependencies of the decomposition of these phenylborate intermediates.

Experimental

Reagent-grade sodium hydroxide was dissolved in distilled, deionized water to provide a 1.5 M stock solution. To this, researchers added diphenylborinic acid as the solid, diethanolamine ester and phenylboronic acid as the pure solid compound. Both phenylborate intermediates came from the Aldrich Chemical Company. The mixtures contained phenylborate intermediates at a starting concentration of approximately 2000 mg/L (~0.01 M). The intermediates were added to the sodium hydroxide solution at room temperature in polyethylene bottles and were allowed to dissolve for one day prior to starting the decomposition tests.

After one day, researchers dissolved copper nitrate hexahydrate, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in distilled, deionized water (~1/3 mL) and added it to a reaction vessel via a 5-mL glass syringe to give a concentration of 10mg/L. They then added approximately 100 mL of phenylborate intermediate containing solution to the reaction vessel using a 5-mL glass syringe.

The reaction vessels differed slightly from those used by Hyder.³ The vessels used in these experiments included a coarse glass frit attached to the end of the glass tube submersed into the solution. This change results in uniformly small air bubbles. Personnel attached the glass tubes to house-supplied air and placed the vessels in pre-heated water baths. House-supplied air flowed at a rate sufficient to provide a continuous stream of air bubbles. The air was pre-saturated with caustic by sparging through 1.5 M NaOH.

Researchers withdrew approximately 4 mL liquid samples from the reaction vessels at selected points during the experiments. Sampling of the vessels occurred after the 100 mL addition of the sodium-hydroxide/phenylborate intermediate solution. These samples served as the "time-zero" concentrations. Personnel filtered all samples using a 0.45 micron filter prior analysis by High Performance Liquid Chromatography (HPLC) using routine protocols.

Experimental Results

The experiments studied copper-catalyzed decomposition of diphenylborinic acid and phenylboronic acid at 25 °C and 40 °C in 1.5 M sodium hydroxide solution under flowing air. Table 1 provides the diphenylborinic acid, phenylboronic acid, and phenol concentrations as a function of time. As previously mentioned, the tests included nominal copper concentrations of 10 mg/L based on the quantity of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ added. Figures 1 through 4 graphically display the decomposition of diphenylborinic acid and phenylboronic acid at 40 °C and 25 °C, respectively.

Decomposition Rates

Researchers tabulated the phenylborate concentration as a function of time in a Microsoft® Excel spread sheet. The software analysis provided pseudo-first order rate constants via the data regression analysis function. Table 2 gives the results of this data analysis along with data derived from Hyder's³ work at 59 °C.

Table 1. Phenylborate Concentration* as a Function of Time

Diphenylborinic Acid

25 °C				40 °C			
<u>Time (h)</u>	<u>2PB</u>	<u>1PB</u>	<u>Phenol</u>	<u>Time (hrs)</u>	<u>2PB</u>	<u>1PB</u>	<u>Phenol</u>
0	8.87	0.17	0.11	0	13.3	3.75	4.67
26	3.88	4.63	4.66	3	12.4	4.58	5.53
47.5	2.82	6.54	10.6	5	11.7	4.97	6.01
71	2.34	6.93	12.1	7	11.1	5.24	6.31
				21.5	7.15	6.94	9.86
				30	6.23	7.09	10.8

Phenylboronic Acid

25 °C			40 °C		
<u>Time (h)</u>	<u>1PB</u>	<u>Phenol</u>	<u>Time (hrs)</u>	<u>1PB</u>	<u>Phenol</u>
0	13.3	0.11	0	18.7	8.46
26	7.83	3.28	3	16.5	10.3
47.5	6.99	5.27	5	15.2	11.4
71	6.69	5.45	7	13.9	13.3
			21.5	7.18	21.4
			30	6.24	22.3

*Concentrations in units of mM.

Table 2. Pseudo-First Order Rate Constants (h^{-1}) for Diphenylborinic Acid and Phenylboronic Acid

Temp (°C)	2PB	1PB
59 ¹	0.188	0.193
40	0.026±0.001	0.0385±0.003
25	0.019±0.004	0.0094±0.003

¹Derived from data found in reference 3.

Fitting a slope to an Arrhenius plot of the natural log of the rate constant versus the inverse temperature will provide an estimate of the activation energy of the decomposition reaction. The results in Table 2 indicate an activation energy of 56 ± 21 kJ/mol and 73.05 ± 0.08 kJ/mol for 2PB and 1PB, respectively.

To compare the results of this work with data previously reported by others, the rate constants need to be adjusted to the same catalyst concentration. Figure 5 shows the data from decomposition studies of 2PB. The relatively large uncertainty in the activation energy and apparent curvature of the 2PB plots indicate potentially two reactions involved in the decomposition. The calculated rate constant at 25 °C exceeds the decomposition of 2PB in either Batch 1 or PVT-1 at ITP.

In the case of phenylboronic acid, the predicted rate constants generated by the data from these tests and that of Hyder³ exceed observations from ITP and other simulant testing except the extrapolated data from Crawford and Peterson⁴ at 25 °C.

Phenol Production

Researchers expected the production of phenol in these flowing air experiments. Previous studies indicated a general trend of phenol production in preference to benzene production in the presence of air. This study confirms that understanding.

In these experiments, the yield of phenol reached 81% and ~ 100% for 1PB at 25 °C and 40 °C, respectively. Although researchers did not examine the 2PB experiments through the complete 1PB decomposition, the results indicate quantitative, sequential steps of $2PB \rightarrow 1PB$ and phenol followed by $1PB \rightarrow$ phenol. The phenol balance was poor (with to high a phenol yield) in the 2PB experiment conducted at 25 °C.

Observations of Color

During these experiments, personnel observed several color changes that may provide insight into this mechanism of decomposition. Phenylboronic acid formed a pink solution under these conditions at both 25 °C and 40 °C. The onset of this color change appeared sooner in the 25 °C experiment. This pink color darkened with time to a ruby red and finally displayed the yellow color exhibited by reagent-grade phenol solutions.

Diphenylborinic Acid, on the other hand, did not show the appearance of this pink color at either the 25 °C or the 40 °C conditions. Diphenylborinic Acid gradually obtained a yellow color consistent with the conversion to phenol. One possible explanation for the lack of color of the 2PB solutions involves diphenylborinic acid reacting with this colored intermediate. The mechanism could occur as:

This proposed mechanism is supported by the observed decomposition rate for 1PB in the decomposition experiments on 2PB. In those tests, the observed rate for 1PB

decomposition is lower (by a factor of 2). A reaction pathway through reaction 3 would suppress the 1PB rate.

Conclusions

This study examined the decomposition of diphenylborinic acid and phenylboronic acid at 25 °C and 40 °C in 1.5 M sodium hydroxide under continuous flowing air. The results of these experiments provide decomposition rate data for use in benzene formation modeling for chemical process in the In-Tank Precipitation facilities. The pseudo-first order rate constants developed from these results measured $0.026 \pm 0.001 \text{ h}^{-1}$ and $0.019 \pm 0.004 \text{ h}^{-1}$ for diphenylborinic acid at 40 °C and 25 °C, respectively. For phenylboronic acid, the pseudo-first order rate constants measured $0.0385 \pm 0.003 \text{ h}^{-1}$ and $0.0094 \pm 0.003 \text{ h}^{-1}$ at 40 °C and 25 °C, respectively. In conjunction with previous work, these results indicate activation energies of $56.2 \pm 21.2 \text{ kJ/mol}$ for the decomposition of diphenylborinic acid and $73.05 \pm 0.08 \text{ kJ/mol}$ for the decomposition of phenylboronic acid.

Color changes observed during the experiments could provide insights into the mechanism for the decomposition of 2PB and 1PB. These observations suggest that further study involving spectroscopic techniques (e.g. Raman spectroscopy or absorption spectrophotometry) could explain the cleavage of the boron-phenyl bond.

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Approvals

Authors:

W. R. Wilmarth, Waste Processing Technology
8-29-97
Date

C. L. Crawford, Waste Processing Technology
8/27/97
Date

R. A. Peterson, Waste Processing Technology
8/27/97
Date

Design Check

D. D. Walker, Waste Processing Technology
8/27/97
Date

Management

S. D. Fink, Manager, Level 4 Manager,
Waste Processing Technology
8/28/97
Date

W. L. Tamosaitis, Level 3 Manager,
Waste Processing Technology
9/9/97
Date

J. T. Carter, Leader
In-Tank Precipitation Flow Sheet Team
9/9/97
Date

M. J. Montini, Deputy Manager
ITP/ESP Engineering
9-5-97
Date

Figure 1. Cu-Catalyzed Decomposition of Diphenylborinic Acid at 40 °C.

Figure 2. Cu-Catalyzed Decomposition of Diphenylborinic Acid at 25 °C

Figure 3. Cu-Catalyzed Decomposition of Phenylboronic Acid at 40 °C.

Figure 4. Cu-Catalyzed Decomposition of Phenylboronic Acid at 25 °C.

Figure 5. Diphenylborinic Acid Rate Constant Data

Figure 6. Phenylboronic Acid Rate Constant Data

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