Acid Hydrolysis of Tetraphenylborate at Elevated Temperature and Pressure

by

J. R. Fowler

E. I. du Pont de Nemours and Company

Savannah River Site

Aiken, South Carolina 29808

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ACID HYDROLYSIS OF TETRAPHENYLBORATE
AT ELEVATED TEMPERATURE AND PRESSURE

Introduction

Sodium tetraphenylborate is used to coprecipitate cesium with potassium in the precipitation process that has been developed to decontaminate waste salt solutions. However, the high organic content of the resulting precipitate prevents direct addition of this precipitate to melter feed containing waste sludge because the level of organic compounds is sufficiently high to reduce many of the waste components to metals. To eliminate this potential problem, three alternatives exist:

1. Remove the organic content from the precipitate by decomposing the tetraphenylborate salts,
2. Incorporate the tetraphenylborate precipitate into a "cesium only" glass, or
3. Use the precipitate to produce gamma sources or heat sources based on Cs-137.

Of these three choices, decomposition of tetraphenylborate salts is preferred if an acceptable process can be developed.

Methods to decompose tetraphenylborate are being investigated by several workers. At my request, T. A. Koch and R. S. Boucher of Petrochemicals Central Research have investigated hydrolysis of potassium tetraphenylborate. Their assistance was requested because of their familiarity with chemical reactions run at elevated temperature and pressure. The equipment and analytical capabilities required for these experiments are also readily available at their laboratory. This report summarizes the results that they have obtained.

SUMMARY

Hydrolysis of tetraphenylborate salts to benzene and inorganic borate is best done at low pH (1-4). Oxygen must be excluded during hydrolysis to avoid undesirable reaction products (phenol, biphenyl). The best results were obtained using these conditions:

1. potassium tetraphenylborate slurried in water was acidified with formic acid (approximately 8 moles HCOOH/mole of tetraphenylborate);
2. oxygen was excluded from the reaction mixture by sparging with nitrogen;
3. the reaction vessel was pressurized to 25 lbs. psig with nitrogen gas;
4. the reaction mixture was heated to 125°C to hydrolyze tetraphenylborate (70 psig at temperature.)

After heating 2 hrs. at 125°C and 70 psig, the mixture was cooled and reaction products were analyzed. Less than 0.1% of the original potassium tetraphenylborate remained in the reaction mixture. Based on the benzene balance for the mixture, approximately 5% of the theoretical yield for benzene is present as phenylboric acid $[(C_6H_5)B(OH)_2]$. The level of biphenyl was at the detection limit in the reaction mixture (approximately 0.002%). Phenylborate esters, observed in other reactions, did not appear to be present in this reaction mixture. This reaction was run using a slurry containing only potassium tetraphenylborate. No other salts or sodium titanate were present.

The reaction was repeated using the KTPB/sodium titanate simulated slurry that we supplied to confirm that these reaction conditions are suitable for our slurry composition. This reaction also proceeded smoothly. A similar product distribution was obtained. In a separate experiment, benzene was allowed to "bleed" out of the reaction vessel as the reaction proceeded. The removal

of benzene as the reaction proceeded did not appear to affect the product distribution.

A simplified flowsheet for hydrolysis of tetraphenylborate based on these results is shown in Figure 1. The benzene stripping operation could conceivably be done in the slurry mixer evaporator in Stage 1 of the DWPF.

A summary of all the reactions are shown in Table I. Appropriate chemical reactions for the best process are shown in Table II. These reactions provide a basis for material balance for the hydrolysis reactions. They do not necessarily reflect the mechanism by which hydrolysis proceeds.

The experiments that we requested are completed. The results provide a basis for a decomposition process based on hydrolysis of TPB. Because of these promising results, I recommend that we install an autoclave to establish specific requirements for a decomposition process based on hydrolysis of TPB at elevated temperature and pressure.

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TABLE IA SUMMARY OF REACTION CONDITIONS FOR
HYDROLYSIS OF TETRAPHENYLBORATE (TPB)

<u>pH</u>	<u>Temperature</u>	<u>Pressure</u>	<u>Comments</u>
>12	320°C	3000 psig	Base stabilizes TPB. 2 hrs. hydrolysis converted approximately 80% TPB to benzene. No phenol or biphenyl detected. Trace of phenylboric acid detected (sodium salt).
1 (HCl)	150°C	90 psig	No TPB detected. Formation of trimeric borate ester oil observed (insoluble in H ₂ O). Ester is condensation product of phenylboric acid.
1 (HNO ₃)	150°C	90 psig	No TPB detected. Phenol detected qualitatively. Trimeric borate ester oil observed. Some nitration of benzene or phenol may have occurred, based on dark color of benzene layer.
2-3 (HCOOH)	125°C	70 psig	Hydrolysis proceeded smoothly with both TPB and simulated slurry. Specific results summarized in body of report.

TABLE IICHEMICAL REACTIONS FOR ACID HYDROLYSIS OF TETRAPHENYLBORATE^a Benzene Benzene + Phenol Benzene + Biphenyl

* M = Na, K, Cs, Rb, Fr

a. These reactions provide a basis for material balance in the hydrolysis process. They do not reflect the mechanism by which hydrolysis proceeds.

FIGURE 1
FLOWSHEET FOR ACID HYDROLYSIS OF TETRAPHENYLBORATE