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ACID-PERMANGANATE OXIDATION OF POTASSIUM TETRAPHENYLBORON (U)

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SUMMARY

Scoping experiments have been performed which show that potassium tetraphenylboron (KTPB) is rapidly oxidized by permanganate in acidic solutions at room temperature. The main products are CO_2, highly oxidized organic compounds related to tartaric and tartronic acids, boric acid, and potassium phosphate (when phosphoric acid is used as the source of acid). One liter of 0.6M $NaMnO_4$/2.5M H_3PO_4 solution will destroy up to 8 grams of KTPB. The residual benzene concentration has been measured to be less than the RCRA limit of 0.5 ppm. Approximately 30% of the organic material is released as CO_2 (trace CO) and 0.16% as benzene vapor. The reaction is well behaved, no foaming or spattering. Tests were performed from .15M to near 1M permanganate. The phosphoric acid concentration was maintained at a concentration at least three times that of the permanganate since an excess of acid was desired and this is the ratio that these two reagents are consumed in the oxidation.

INTRODUCTION

Analytical Development Section (ADS) support of the Waste Farm ITP process will produce residues containing alkali tetraphenylboron (TPB) and trace benzene in solution. These compounds and other RCRA listed hazardous materials must be removed before these waste solutions can be discarded to the SRTC High Level Waste Tanks. Other methods have been developed to remove hazardous metals such as lead, silver, mercury, and cadmium but a chemical process to remove benzene and its precursors, such as TPB, needs to be developed. Such a chemical process would need to destroy the TPB, benzene, and related compounds without the release of a large fraction of the TPB, as benzene, into the chemical exhaust ventilation system. Since the hydrolysis of TPB to benzene and boric acid is very slow at room temperature a process was sought that could accomplish the destruction of the phenyl groups of TPB at room temperature, before any benzene could even be produced. Other characteristic requirements of such a process are relative quickness, well behaved (no spattering or foaming), reaction in a single "accumulation" vessel (wouldn't need a permit), and ease of transformation to a state for further processing.

One chemical process that could possibly fit the above criteria was permanganate oxidation in acidic media. Permanganate is well known to rapidly oxidize carbon-carbon double bonds at room temperature. The reaction rate can be controlled by using a weak self-buffering acid such as 2.5M phosphoric acid and relatively dilute permanganate. Reaction conditions were sought which would sufficiently complete the oxidation in a few minutes to allow further processing. The excess permanganate can easily and quickly be destroyed with oxalic acid solution at room temperature.

This study has been performed to define the range of permanganate and phosphoric acid concentrations where TPB can be destroyed to benzene levels below the RCRA limit, .5 ppm, at room temperature. This study was devised to determine the percentages of CO_2, CO, and benzene released as gas during the oxidation, thus allowing a carbon balance and a general characterization of the organic compounds left in solution.

EXPERIMENTAL

The original research plan was to use analysis support from Analytical Development Section (ADS) for trace benzene analysis and support from Intermediate Waste Technology (IWT) for offgas characterization, using a gas chromatograph (GC). The loss of GC support early in the research program necessitated the development of an on-line quantitative gas analysis process for CO_2 and CO. A method of checking this system was also developed using sodium oxalate and concentrated sulfuric acid to produce a quantitative amount of CO and CO_2 (50 mole% each). The quantitative measurement of CO_2 was performed using a weighed amount of ascarite, NaOH on a solid support. A flow-diagram of the reaction-analysis system is shown in Figure 1. The peristaltic pump was set to deliver 50 ml/min. of air through the system. The air was first dried and scrubbed of CO_2, with ascarite, just prior to entering the peristaltic pump. The air then swept the reaction vessel system of gaseous products. A measured amount of deuterated benzene was added to the system immediately after addition of the potassium tetraphenylboron (KTPB) sample to calibrate the dry-ice trap, used to measure benzene loss as vapor. Drierite, anhydrous calcium sulfate, is used to remove the last traces of water before the CO_2 produced in the oxidation enters the first ascarite container. The ascarite bottle could be disconnected and weighed prior and during the actual oxidation reaction (the pump was turned off and the system sealed while the bottle was weighed). The system was checked for stability with repeated weighings prior to addition of KTPB. Any CO offgas would then be oxidized to CO_2 by the oxygen in the air on the Pd/Kieselguhr catalyst, maintained at 140°C. This newly produced CO_2 was then absorbed on another preweighed bottle of ascarite. The air sparge flow-rate was measured using an inverted burette.

Measurement of CO and CO_2

A quantitative amount of CO and CO_2 can be produced by the dehydration of oxalate in concentrated sulfuric acid.

$$C_2O_4^{2-} + 2H^+ \xrightarrow{H_2SO_4} H_2O + CO + CO_2$$

Heating to near 120°C for two hours is needed for quantitative generation. Even when the reaction is not complete the mole production of CO and CO_2 is equal. The measured weights of CO (as CO_2) and CO_2 were always found to be nearly the same, ±2%, verifying that the Pd/Kieselguhr catalyst and both traps were working correctly. The reaction was considered complete when the weights of the ascarite traps became relatively constant for two hours. The measured values for CO and CO_2 had an accuracy of about ±2%.

Measurement of Benzene Release

The dry-ice trap was used to measure the quantity of released benzene vapor. The trap was standardized by adding a measured amount of deuterated benzene (C_6D_6) through the septum, between the reaction vessel and dry-ice trap, just after addition of the KTPB to the oxidizing solution. The assumption is that the trap will be equally as efficient for absorbing the deuterated benzene as for any benzene released from the oxidation. When the reaction was complete, approximately 6 ml of absolute ethanol was added to the trap to dissolve the trapped benzene and deuterated benzene. The ethanol was then sent to ADS for trace benzene analysis. The ratio of the measured benzene to measured deuterated benzene times the amount of deuterated benzene added gave the total amount of benzene released in the oxidation. This value was compared to the maximum benzene possible from the KTPB added to get a percentage released.

Permanganate Consumed

The permanganate concentration in the oxidizing solution both prior and after the oxidation was measured using the McBride procedure[1]. This procedure uses the permanganate solution to titrate a 1.5M sulfuric acid solution containing a weighed amount of sodium oxalate. A persistent purple coloration marks the end-point of the titration. The permanganate concentration can easily be measured to an precision of ±.002M by this method and triplicate titrations.

Total Carbon In Solution (TOC)

Samples of the oxidizing solution were sent to ADS for TOC analysis. The values given by this method represent the quantity of organic material that can be oxidized completely to CO_2, which is the species actually measured, in persulfate at elevated temperature. Not all organic compounds will be fully oxidized by this process. Any carbon not accounted for as TOC, benzene vapor, CO_2, or CO is assumed to be in solution as highly oxidized, stable, organic material.

OXIDATION CHEMISTRY

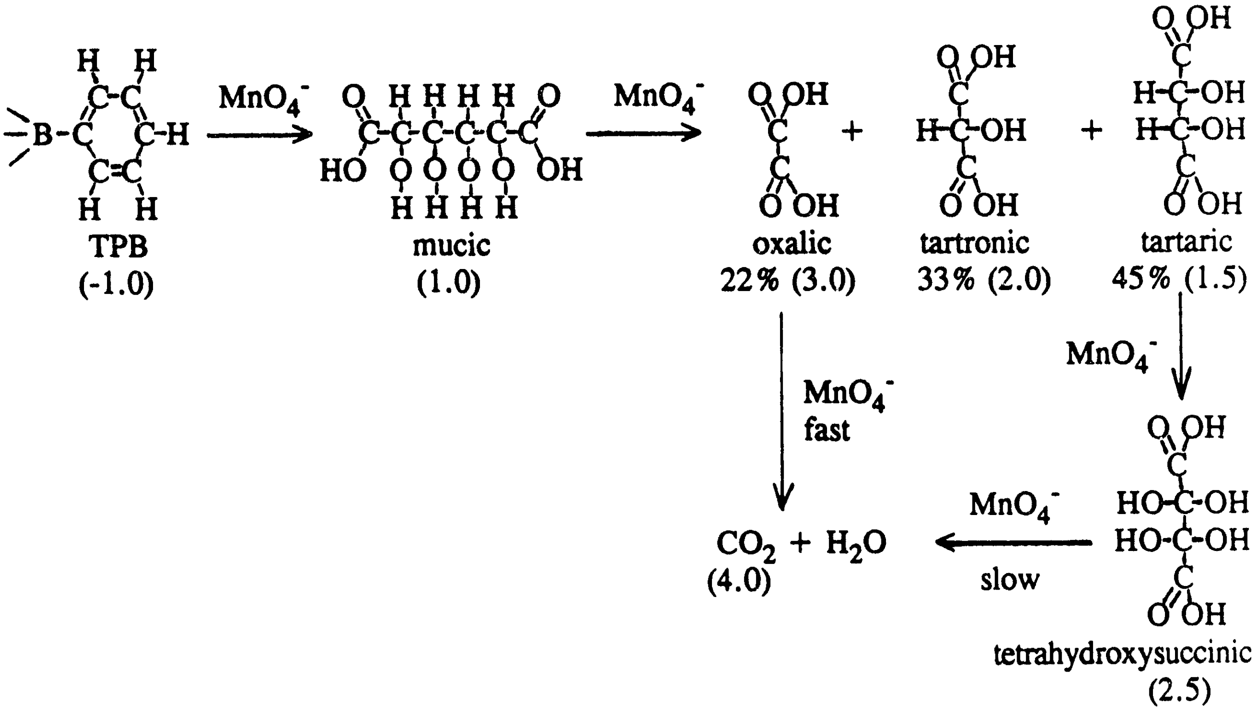
Permanganate Oxidation of KTPB

The oxidation of benzene, or TPB, by permanganate uses three moles of acid for every mole of permanganate.

$$6MnO_4^- + 18H^+ + C_6H_6 \longrightarrow 6Mn^{2+} + 12H_2O + 6CO_2 \qquad (1)$$

In phosphoric acid the permanganate is completely reduced to Mn^{2+} (in base MnO_2 is the final product). The oxidation of each carbon-carbon double bond of benzene requires the transfer of two electrons. Since manganese can't assume the +5 oxidation state, reaction with benzene is second order[2]. This requires that two molecules of permanganate approach each carbon-carbon bond simultaneously for oxidation. Planer organic compounds such as benzene accommodate oxidation by allowing approach from two sides, which is probably why this reaction is so rapid at room temperature. Other organic compounds which can attain a planer configuration, such as oxalic acid, also react rapidly. Permanganate in acid solution oxidizes all primary carbon atoms to carboxylic acids and nonprimary carbon atoms to first alcohols and more slowly to ketones[3,4].

Permanganate attack on the phenyl (benzene) groups of TPB starts by oxidation of the three carbon-carbon double bonds to alcohols. Breakage of one of the carbon-carbon bonds in the resulting ring and oxidation of the primary, end, carbon atoms to carboxylic acid groups, which should be rapid[3,4], results in mucic acid.



Attack on the three inner carbon-carbon bonds of mucic acid should be quick relative to the end bonds due to steric hindrance of the later. Assuming these three bonds are attacked in equal proportion, with subsequent oxidation of the resulting primary carbon atoms; then oxalic, tartronic, and tartaric acids should be produced in near equal molar amounts. The oxalic, tartronic, and tartaric acids represent 22, 33, and 44% of the carbon in solution respectively. The numbers above in parenthesis are the average charge per carbon atom for each compound.

The oxalic acid is rapidly oxidized to CO_2 and water. The tartronic acid should be relatively stable to further attack due to steric hindrance (mainly due to repulsion of the carbonyls with the oxygens of the permanganate). The middle carbon atoms of tartaric acid are a little less hindered and can be further oxidized to tetrahydroxysuccinic acid. Final oxidation to oxalic acid should be relatively slow (which then rapidly produces CO_2 and water). The above outline fits the theory[2,3,4] and the data (Table 1) which shows that 22±2% of the organic carbon is oxidized to CO_2 in the first few hours, probably in the first few minutes. Letting the solution set overnight or increasing the temperature produces more CO_2. Heating the solution to 95°C for three hours converted 70.5±2% of the carbon to CO_2. This probably represented most of the tartaric acid and a small portion of the tartronic acid.

Decomposition of Acidic Permanganate Solutions

The decomposition of permanganate in dilute acid solution proceeds slowly at room temperature.

$$4MnO_4^- + 12H^+ \longrightarrow 4Mn^{2+} + 5O_2 + 6H_2O \qquad (2)$$

The decomposition rate was measured as 0.37%/day in approximately 1M permanganate and 2.0M phosphoric acid at room temperature. This rate drops quickly with decreasing acid and permanganate concentration. Decomposition of a 0.6M $NaMnO_4$/2.5M H_3PO_4 solution should be about four times slower.

Oxalic Acid Reduction of Permanganate

Reduction of permanganate with oxalic acid proceeds through a radical mechanism. The reaction is catalyzed by Mn^{2+} and therefore requires an induction period with fresh solution.

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \qquad (3)$$

If a significant amount of Mn^{2+} is already in solution, due to subsequent oxidation of KTPB, then the reaction should proceed quickly from the beginning at room temperature.

DISCUSSION

Residual Organic Compounds

A significant fraction of the organic carbon is left in solution, >70%, when KTPB is oxidized in acidic permanganate at room temperature. The product solution should contain oxidized compounds similar to tartronic and tartaric acids. A calculation of the average charge per carbon atom remaining in solution can be used to verify this last statement and this can be done if the beginning and end permanganate concentrations are known accurately. Subtracting off 5, 3, and 0 electrons respectively for every CO_2, CO, and benzene molecule produced in the oxidation and using the data from Table 1, a value of 2.24 is obtained. This value implies compounds similar to tartronic and tetrahydroxysuccinic acid which have average charges of 2.0 and 2.5. These two compounds were expected from the theory[2,3,4] and should be stable and are very water soluble[5].

Benzene Vapor Loss

The loss of TPB as benzene vapor is small, 0.16%, which was expected for room temperature oxidation. Initial oxidation of the phenyl groups (benzene) of KTPB produces alcohol groups on the carbon ring (described earlier). These alcohol groups make the organic molecule less volatile and more water soluble. Only the KTPB that is able to hydrolyze (due to localized heating of the solution produced by the oxidation) will be able to escape.

$$KB(C_6H_5)_4 + H_2O \longrightarrow KB(C_6H_5)_3OH + C_6H_6 \text{ (benzene)}$$

Most of the heat of reaction, which is significant (3,865 kcal/mole TPB)[6], is lost to the surrounding solution.

Residual Benzene in Solution

The residual benzene in solution was below the RCRA limit of .5 ppm for room temperature oxidation, .190 and .071 ppm (Table 1). Other benzene related compounds, such as phenol, should also have been destroyed since permanganate has a strong affinity for carbon-carbon double bonds[2,3,4]. Benzene, TPB, and related aromatic compounds should not survive in acidic permanganate solutions above RCRA limits.

Treatment of Solid KTPB

The oxidation rate of KTPB is second order in permanganate concentration and first order in acid[2,3,4]. The oxidation rate with permanganate concentrations above 1M, with at least a three fold excess of acid, is quite rapid. The rate for a 0.6M $NaMnO_4$/2.5M H_3PO_4 is at least 4.5 times slower and is relatively well behaved. The oxidation rate should be sufficiently fast and complete down to at least .15M permanganate for further processing in about ten minutes. One liter of 0.6M $NaMnO_4/2.5H_3PO_4$ will destroy up to 8 grams of solid KTPB. This is the amount of KTPB expected to be in one sample sent from ITP for analysis. The residual permanganate should be about .15M and can be destroyed with about 600 ml of 0.8M oxalic acid solution. The pH of the solution after destruction of the excess permanganate should be between 2 and 3[7].

Treatment of Dissolved TPB and Benzene

Oxidation of benzene and related compounds dissolved in solution should react similarly to solid KTPB. Expected differences are a reduced benzene vapor loss during oxidation and slightly more foaming of the solution due to evolved product gases. Oxidation of solid KTPB occurs at the surface of the solution, KTPB floats, resulting in easier escape of the product gases.

When treating solutions containing dissolved TPB or benzene it is important to neutralize the solution and remove all compounds that will destroy the acid or permanganate. Compounds which will possibly be present and cause problems are base, nitrite, carbonate, and oxalate[8]. Acidifying the solution to a pH of 3 and letting the solution set stirring should remove the carbonate, nitrite (as nitrous acid), and oxalate (which will be destroyed by the generated nitrous acid). The waste solution can then be added directly to the permanganate solution. If a gram per liter of TPB or less is dissolved in the waste solution, approximately three liters of waste solution can be added per liter of permanganate solution. This equates to about a 33% increase in waste volume.

Safety of Permanganate Oxidation Process

Permanganate solids and concentrated solutions are strong oxidizers, especially in acidic solution. The permanganate oxidation of TPB compounds can be performed safely as long as the appropriate safety precautions are taken and low permanganate and acid concentrations are used[9]. Low acid concentrations can be maintained by using a weak self-buffering acid such as H_3PO_4 or $NaHSO_4$. The heat produced in the oxidation of 8 grams of KTPB should be about 52 kcal[6], which is less than the maximum 86 kcal due to incomplete oxidation. Much of the heat produced is lost to the product gases, CO_2 and H_2O. The solution temperature has been found experimentally to increase to only about 40°C, far from the maximum 110°C. A total of 3.5 liters of gas should be released from the oxidation of 8 grams of KTPB. This release occurs over about two minutes in a controlled fashion. If a higher concentration for either permanganate or acid is desired then tests should be performed to determine the rate, mildness (or violence), of the reaction at the new reaction conditions. A safety analysis has been performed for this oxidation process[9].

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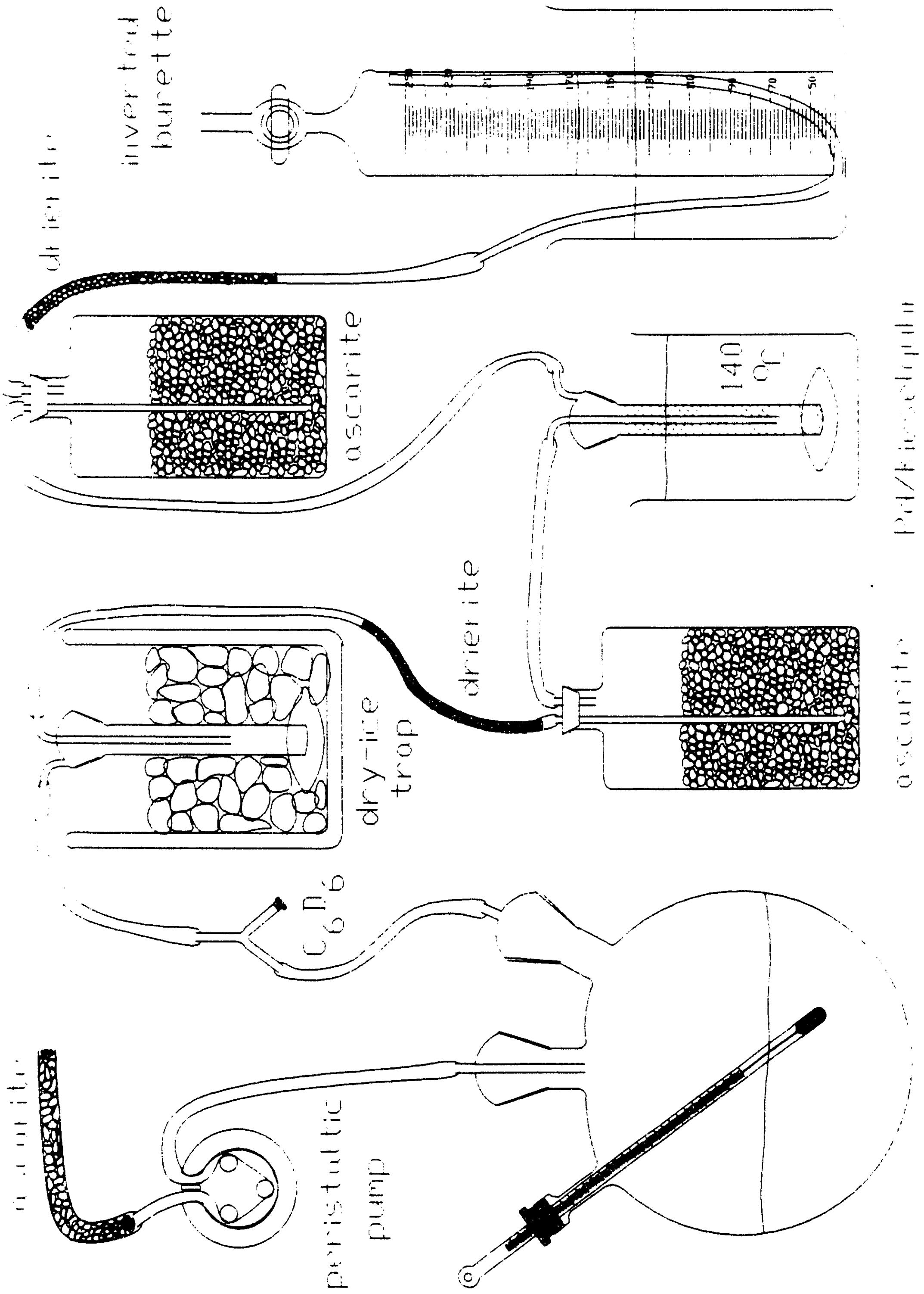
TABLE 1

KTPB Oxidation by Permanganate in Dilute Phosphoric Acid (1.5-2.0M)

Organic (grams)	$[MnO_4^-]$ initial/final	T(°C)	$\%CO_2$	%CO	C_6H_6 sol. (ppm)	$\%C_6H_6$ vapor	%C sol. (TOC)
KTPB (1.178 ±.004)	~1.0 (initial) 500 ml	23	-	-	.190	-	-
	.43±.01 (final)	70	60±5	-	.180	-	-
KTPB (.148 ±.002)	.200±.001 (initial) 250 ml	23	22.2±2	-	-	-	-
	-	23	33.4±2 (20 hrs)	-	-	-	-
	.158±.002 (final)	47	50.6±2	1.8±2	.071	0.16	38.4 (55 ppm)
		95	70.5±2	6.3±2	-	-	-

FIGURE 1


inverted burette
drierite
ascarite
140 °C
Pd/kieselguhr
drierite
ascarite
dry-ice trap
C_6D_6
ascarite
peristaltic pump

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