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HYDROGEN GENERATION BY RADIOLYSIS OF TETRAPHENYLBORATE SOLUTIONS AND SLURRIES (U)

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

SUMMARY

The yields of hydrogen from irradiation of tetraphenylborate (TPB) solid salts, aqueous solutions and slurries have been measured. The results are summarized as follows.

- No hydrogen was detected from irradiation of either sodium tetraphenylborate (NaTPB) or potassium tetraphenylborate (KTPB) solid salts. Based on detection limits the hydrogen G values were < 0.025 molecules per 100 eV.

- No hydrogen was detected when irradiated solid NaTPB salts or irradiated NaTPB slurries were dissolved in water. Based on detection limits the hydrogen G values were < 0.01 molecules per 100 eV.

- All radiolytic hydrogen yields for the solutions and slurries were less than 0.46 molecules/100 eV, which is the maximum G value for H_2 production from radiolysis of water.

- Hydrogen yields from TPB slurries in concentrated salt solutions in which the sum of nitrate and nitrite concentrations was greater than 1 M were all ≤ 0.11 molecules/100 eV.

- The G value for free hydrogen production decreases as nitrate and nitrite concentrations increase. The correlation is similar to one based on nitrate concentrations used to predict hydrogen production rates in other waste tanks in the F and H Tank Farms at the Savannah River Site.

- The effect of minor components on radiolytic hydrogen production was found to be insignificant. The added components were formate, titanate, sludge, mercury, and a mixture of alcohols that are known to be present in the In-Tank Precipitation (ITP) process slurries.

In this study a correlation is presented based on literature data for either nitrate or nitrite systems, as well as our measured hydrogen production data for nitrate plus nitrite systems. Using this correlation one can predict maximum radiolytic hydrogen production from such systems as the TPB high salt-containing slurries found in the ITP process.

INTRODUCTION

This report is a summary of experimental results on radiolytic hydrogen yields from tetraphenylborate (TPB) slurries related to the In-Tank Precipitation (ITP) process. The yields are presented as "G values" in units of molecules per 100 eV of absorbed energy. If the radiolytic dose rate is known, the combination of the G value and dose rate gives the rate of hydrogen production.

Radiolytic hydrogen production rates are required in safety calculations that predict hydrogen generation in the ITP waste-tank vapor space. Volatile gases generated in the ITP process are purged from the tank vapor space by an active ventilation system. However in the event of an accident or mechanical breakdown of the ventilation system, hydrogen could accumulate in the tank vapor space. Knowing the dose rate, slurry compositions and the G value for the composition allows one to calculate the accumulation rate for hydrogen and thus calculate its contribution to the combustible gas concentration.

This report presents H_2 G values measured on the following systems.

1) Solid Na or K salts of tetraphenylborate (Na/KTPB)
2) Aqueous solutions containing soluble TPB^- without TPB solids present
3 Aqueous slurries in concentrated salt solutions containing 1-10 wt % of Na/KTPB solids

During most of the ITP cycle, significant amounts of nitrate, nitrite, and other soluble ions are present in the waste. It is known that the G value for hydrogen production decreases as the concentration of nitrate or nitrite increases in aqueous solutions.[1-5] In the present work, hydrogen production from radiolysis of aqueous solutions containing equal-molar mixtures of nitrate and nitrite with no dissolved organics present is also reported. This data as well as similar nitrate or nitrite data obtained from the literature[1,4] is used to correlate radiolytic hydrogen production from aqueous mixed nitrate/nitrite-containing solutions including the TPB slurries relevant to the ITP process. Correlations of radiolytic hydrogen production with nitrate concentrations are currently used to predict hydrogen production rates in other waste tanks in the F and H Tank Farms at the Savannah River Site. The results of this study are discussed below. Experimental methods are detailed in Appendix A.

RESULTS AND DISCUSSION

Radiolytic Decomposition of Solid NaTPB and KTPB Salts

Typical ITP waste slurries can contain up to 10 wt % insoluble TPB solids. The solid NaTPB and KTPB salts decompose when irradiated either as dry salts or as ~1-10 wt % slurries. Results from experiments on radiolytic destruction of NaTPB solids and slurries containing 6-8 wt % KTPB are shown in Table 1. Some of the experimental information is given in Table 1 and further experimental details for these and other experiments presented in this study are given in Appendix A. The experiments involving irradiation of solid NaTPB salts were performed to investigate the radiolytic yields for loss of TPB by direct irradiation effects. Results for the solid NaTPB sample were obtained in this laboratory. The loss of solid NaTPB from irradiation of 2-gram quantities in open glass vessels was linear over a 60 Mrad dose. Results for the 6-8 wt % KTPB slurries shown in Table 1 are adapted from published data concerning experiments conducted at the University of Florida.[6] These previously published results for the KTPB slurries shown in Table 1 of this report are presented here for comparison purposes to our results for the solid NaTPB salts.

The yields shown in Table 1 are expressed as G values. The G value is defined as the number of molecules produced or consumed per 100 eV of energy absorbed. As shown in Table 1, the G values for KTPB loss in the 6-8 wt % slurries can be expressed either on a dose to slurry or dose to solids basis. The G value yields expressed on a dose to solids basis are ~10X higher than on a dose to slurry basis for the KTPB slurries. This is because the dose to solids G value calculation assumes that the 6-8 wt % of KTPB solids in the slurry directly absorb only 6-8 % of the total ionizing radiation absorbed by the entire slurry system; this dose to solids calculation also assumes that only direct energy absorption by the KTPB solid causes radiolytic loss of TPB. As pointed out and discussed in detail in **Ref. 6**, loss of KTPB solid in the KTPB slurries is likely due to a combination of direct and indirect radiation absorption processes. Loss of solid KTPB by the direct effect would involve absorption of radiation by the solid KTPB salt. Loss of KTPB solid by the indirect effect would involve dissolution of the KTPB salt to maintain its equilibrium with a small portion of soluble TPB^-; the soluble TPB^- could be consumed indirectly in solution by reactions involving the dissociation products of water radiolysis.

The results of Table 1 (see dose to solids G values) indicate that damage to the dry NaTPB was approximately two times greater than to solid KTPB in the slurry. This residual difference between the G values may be due to the difference in availability of oxygen in the two systems. The NaTPB solids were irradiated in open-air glass containers for relatively lower doses up to 60 Mrad. The KTPB slurries were irradiated in small test tubes fitted with ground glass seals. It was postulated that the KTPB slurries became anoxic during the rather large accumulated doses of 160 or 480 Mrads.[6] The presence of oxygen is known to magnify the radiation damage to some organic compounds.[7]

TABLE 1. Radiolytic Decomposition of NaTPB or KTPB Solids

TPB System	Dose Range (Mrad)	G(-Na/KTPB) Value (molecules/100 eV)	
		(Dose to Slurry)[a]	(Dose to Solids)[b]
NaTPB Solid Salt[c]	0-60		4.3
Washed 6 wt % KTPB[d] Slurry	0-160	0.13	2.17
Washed 6 wt % KTPB[d] Slurry	0-480	0.12	2.00
Unwashed 8 wt % KTPB[e] Slurry	0-480	0.18	2.25

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[a] The dose to slurry G(-KTPB) values calculated based on the mass of slurry (solids plus liquid) present. These are the G(-KTPB) values reported in **Ref. 6**.

[b] The dose to solids G(-NaTPB) or G(-KTPB) values calculated based on the fraction of energy absorbed by the mass of solids (either NaTPB or KTPB) present.

[c] Dry 2-gram quantities of NaTPB solid salts irradiated in open glass vessels at SRTC. Solids dissolved in ~20 mL of water after irradiation. The remaining NaTPB was measured gravimetrically by precipitating and isolating with excess potassium cation.

[d] Washed KTPB slurries contained ~3.3 M $NaNO_3$, 1.0 M $NaNO_2$, and 1.3 M NaOH that were washed in a final step to remove adsorbed and occluded salts. Residual KTPB analyzed by liquid chromatography after dissolving the solid in acetonitrile (See **Ref. 6** for details).

[e] Unwashed KTPB slurries contained ~3.3 M $NaNO_3$, 1.0 M $NaNO_3$, and 1.3 M NaOH. Residual KTPB analyzed by liquid chromatography after dissolving the solid in acetonitrile (See **Ref. 6** for details).

Radiolytic Hydrogen Production From Decomposition of Solid NaTPB and KTPB Salts

Solid NaTPB and KTPB salts were irradiated to determine the effects of direct absorption of radiation by the solids on hydrogen production. The resulting measurements of volatile hydrogen are shown in Table 2. No hydrogen was detected in the gas space above any of the irradiated solid TPB samples that were irradiated and sampled in sealed glass containers. In these particular experiments no efforts were made to determine the yields for loss of either the solid NaTPB or KTPB salts. The $G(H_2)$ values presented in Table 2 were calculated using the gas chromatography instrumental detection limit of ~15 ppm by volume for H_2, the mass irradiated, absorbed dose, void volume, and the ideal gas law.

Similar results involving no detectable hydrogen were found for both the dissolution with water of irradiated NaTPB solid salts and irradiated slurries. The various NaTPB slurries that were irradiated and dissolved in water to investigate the possible production of 'trapped' hydrogen are shown in Table 3. In these dissolution experiments any volatile hydrogen produced from the irradiated aqueous slurries was removed before the slurries were sealed and dissolved with water.

The negligible yields of H_2 from irradiation of the solid TPB salts, either as volatile hydrogen (See Table 2) or as trapped hydrogen (See Table 3) indicate that any direct effects of radiation on solid TBP salts should not contribute to any radiolytic hydrogen production from irradiation of the ITP aqueous salt slurries containing solid TPB salts. Radiolytic hydrogen production results from these tests were expected due to the aromaticity of the TPB molecule. For instance, it is known that pure liquid aromatic hydrocarbons are much more resistant to direct radiation damage with respect to hydrogen production than pure liquid aliphatic hydrocarbons.[8-10]

TABLE 2. Volatile Hydrogen from Irradiation of NaTPB or KTPB Solid Salts

	Mass (grams)	Na/KTPB	Dose (Mrad)	$G(H_2)$ Value (molecules/100 eV)[a]
Air-dried	1.55	Na	1.0	<0.025
Oven-dried[b]	1.49	Na	1.0	<0.025
Air-dried	1.53	K	1.0	<0.025
Oven-dried[b]	1.51	K	1.1	<0.025

[a] The $G(H_2)$ values calculated based on the mass of solid salts irradiated, dose absorbed, and the gas chromatography experimental detection limit of ~15 ppm by volume for H_2.

[b] Oven-dried samples dried at 105°C for ~12 hours prior to irradiation to insure no water was present.

TABLE 3. Trapped Hydrogen from Irradiated Simulated Slurry Compositions.[a]

Salt Conc. (molar Na^+)	Waste Type[b]	Solids (wt %) K/NaTPB	Dose Range (Mrad)	$G(H_2)$ Value (molecules/100 eV)[c]
5.0	average	0/1.0	0.5-50	<0.01-0.001
5.0	average	3.4/1.6	0.5-50	<0.01-0.001
5.0	average	5.3/0	0.5-50	<0.01-0.001
5.0	average	0/5.4	0.5-50	<0.01-0.001
6.0	high nitrate	3.6/1.8	0.5-50	<0.01-0.001
2.0	high nitrate	3.5/0.7	0.5-50	<0.01-0.001
7.4	high hydroxide	3.0/2.3	0.5-50	<0.01-0.001

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[a] Identical results, i.e. no evidence for production of trapped hydrogen, were found for irradiated NaTPB solids that were dissolved with water.

[b] See Table 5 in latter section of this report for details on the various typical waste slurry types.

[c] The range of $G(H_2)$ values calculated based on the mass of solid salts or slurries irradiated, doses absorbed, and the gas chromatography experimental detection limit of ~15 ppm by volume for H_2.

Aqueous Solutions Containing Dissolved TPB^- Without TPB Solids Present

Concentration Effects

Homogeneous aqueous solutions containing 0.0005-0.5 M TPB^- were irradiated and the radiolytic hydrogen yields were measured. The TPB^- concentration range was varied from 0.0005 M to 0.5 M to cover the range expected in the ITP process. The TPB^- was completely soluble at all of these concentrations. The hydrogen yields are shown in Table 4, Expts. #1-4. For the inert atmosphere tests, oxygen was removed by purging with nitrogen. Duplicate samples were irradiated to a single dose of 1 Mrad. The solutions also contained ~$1x10^{-4}$ M Br^- to protect the H_2 by scavenging the primary OH radical produced from water dissociation.[9] The TPB^- itself could also serve to scavenge OH radical as shown in reaction B1-26 of Table B1 in Appendix B. (Reactions relevant to water radiolysis, hydrogen production, and various solutes such as nitrate, nitrite and tetraphenylborate are collected in Table B1 of Appendix B). After the irradiations, gas pressure increases within the vials were found to be small (+0.2 to +0.5 psig).

The $G(H_2)$ values for irradiation of the 0.0005-0.5 M TPB^- solutions containing $1x10^{-4}$ M Br^- in Expts. #1-4 of Table 4 were all < 0.46 molecules/100 eV. Hydrogen yields for the

0.0005-0.05 M TPB^- solutions were similar, in the range of $G(H_2) = 0.40-0.45$. The lower yield of 0.33 for the 0.5 M TPB^- solution appears to be significantly lower than hydrogen yields for the less concentrated 0.0005-0.05 M TPB^- solutions. At a concentration level of 0.5 M the TPB^- could possibly be scavenging the precursors to molecular hydrogen (e_{aq}^-, H). Additionally it can be shown from electron fraction calculations[9] that at 0.5 M, the dissolved TPB^- itself would absorb ~12 % of the total energy deposited in the TPB^-/water system. From the experiments above on irradiated solid TPB salts, insignificant amounts of hydrogen production are expected by this direct radiation absorption process.

Effects of Gas-Purging, Added Hydroxide, Added Nitrate or Nitrite

Solutions of 0.05 M TPB^- have been irradiated in sealed vials under several different solution conditions including pre-irradiation-gas-purges with nitrogen and oxygen, added hydroxide, and added nitrate or nitrite. The $G(-TPB^-)$ and $G(H_2)$ values from these Expts. #6-13 are also shown in Table 4. In all of the solutions shown in Table 4 the TPB^- was completely dissolved forming homogeneous solutions with no solids present. The data for experiment #5 in Table 4 is adapted from previously published radiolysis studies on 0.05 M aqueous solutions of tetraphenylborate,[11] and is included for comparison. Loss of the parent TPB^- was gravimetrically determined by filtering the aqueous samples to remove any insoluble organic solids formed as a result of irradiation and treating the filtrate with excess potassium ion to precipitate the remaining soluble TPB^-. Depletion of oxygen was measured in the oxygenated and aerated systems. The $G(-O_2)$ values, which were calculated from the change in oxygen content of the gas space above the liquids, are also shown in Table 4. The radiolytic yields of the nitrate and nitrite anions, as determined by ion chromatography (IC), are included in Table 4 for the aerated, neutral TPB^- systems containing either 0.1 M nitrate or 0.1 M nitrite (see Expts. #12 and #13, respectively). Gas pressure increases within the vials in the N_2-saturated system were in the range of +0.2 to +0.6 psig. These pressures result from radiolytic production of volatile gases that have been experimentally measured such as hydrogen, benzene, and 1,4-cyclohexadiene. Gas pressure decreases within the vials in the O_2-saturated system were in the range of -1.4 to -2.2 psig. Pressure changes were all < +0.5 psig in the various aerated systems.

TABLE 4. Radiolytic Decomposition of TPB^- and Radiolytic Hydrogen Production from Aqueous Solutions Containing Soluble Tetraphenylborate

Expt. #	$B(C_6H_5)_4^-$ (M)	Atmosphere	$G(-TPB^-)$ (molecules/100 eV)	$G(H_2)$ (molecules/100 eV)	
1[a]	0.50	N_2		0.33±0.00	
2[a]	0.05	N_2		0.45±0.03	
3[a]	0.005	N_2		0.38±0.03	
4[a]	0.0005	N_2		0.41±0.05	
5[b]	0.05	Air		0.46	
6[c]	0.05	N_2	2.36	0.46	
7[c]	0.05	O_2	2.51	0.36	$(G(-O_2)=2.5)$
8[c]	0.05	Air(20cc)	2.19	0.45	$(G(-O_2)=0.6)$
9[d]	0.05	Air(10cc)	2.26	0.42	$(G(-O_2)=0.5)$

Expt. #	$B(C_6H_5)_4^-$ (M)	Atmosphere	OH^- (M)	$G(-TPB^-)$ (molecules/100 eV)	$G(H_2)$ (molecules/100 eV)	
10[c]	0.05	Air	0.1	2.08	0.38	$(G(-O_2)=0.5)$
11[c]	0.05	Air	0.5	1.89	0.40	$(G(-O_2)=0.7)$

Expt. #	$B(C_6H_5)_4^-$ (M)	Atmosphere	NO_3^- (M)	NO_2^- (M)	$G(-TPB^-)$ (molecules/100 eV)	$G(H_2)$ (molecules/100 eV)	
	0.05	Air	0.1	0.0	1.73	0.27	$(G(-O_2)=0.5)$ $(G(-NO_3^-)=4.2)$ $(G(NO_2^-)=3.4)$
	0.05	Air	0.0	0.1	0.92	0.31	$(G(-O_2)=0.7)$ $(G(-NO_2^-)=3.5)$ $(G(NO_3^-)=<0.1)$

[a] Sets 1-4: Duplicate 40-mL N_2-purged samples containing $1x10^{-4}$ M Br^-, irradiated to single dose of 1 Mrad.

[b] Data from (Gupta *et al.*, 1991).[11]

[c] Sets 6-8, 10-11: Duplicate 40-mL samples irradiated at three different doses in the range of 0-2 Mrad.(See Figures 1,2 and 3).

[d] Set 9: Duplicate 50-mL samples irradiated at three different doses in the range of 0-2 Mrad.

[e] Sets 12-13: Duplicate 40-mL samples irradiated at two different doses in the range of 0-1.8 Mrad. (See Figures 1-5).

Loss of Tetraphenylborate

Loss of tetraphenylborate was linear with absorbed dose in the range of 0-2 Mrad for all of the 0.05 M TPB^- systems as shown in Figure 1. The $G(-TPB^-)$ values are in the range of 2.2 to 2.5 for the neutral TPB^- systems (See Expts. #6-9 of Table 4). Loss of TPB^- was slightly lowered in the presence of 0.1 M OH^- and 0.5 M OH^-. Loss of TPB^- was also lowered in both the nitrate and nitrite systems. The nitrate/TPB^- and nitrite/TPB^- systems are discussed in detail later in this report. $G(-TPB^-)$ yields for loss of soluble TPB^- such as those reported in Table 4 have not been reported in any of the previous published studies on radiolysis of aqueous tetraphenylborate[6,11-12] As mentioned above and detailed in **Ref. 6**, the G values measured for loss of KTPB from the slurries are likely indicative of a combination of direct and indirect radiation absorption processes. The TPB^- loss yields shown in Table 4 for 0.05 M TPB^- solutions involve only indirect processes in which the radiolytic dissociation products from water attack the soluble TPB^- in solution. These $G(-TPB^-)$ values of less than 2.5 indicate that TPB^- reacts with less than 50 % of the total available primary radical species from water radiolysis; their combined yields are $(G(OH)=2.7 + G(e_{aq}^-)=2.6 + G(H)=0.5) \approx$ 5.8 molecules/100 eV.[9]

The magnitude of the $G(-TPB^-)$ values in the range of ~2.2 to 2.5 molecules/100 eV are similar to the yield of the hydroxyl radical, $G(OH) = 2.7$,[9] from the radiolytic dissociation of water. The present data supports previous pulse radiolysis studies in which it was concluded that TPB^- readily reacts with OH with a rate constant of $\sim 6 \times 10^9\ M^{-1}s^{-1}$ and that TPB^- is rather unreactive with the hydrated electron, e_{aq}^-, i.e. $k(TPB^- + e_{aq}^-) < 1 \times 10^6\ M^{-1}s^{-1}$.[12] Data reported here also suggests that TPB^- does not react effectively with the hydrogen radical ($G(H)=0.55$ from water radiolysis)[9] since one could expect maximum $G(-TPB^-)$ yields as high as ~3.3 ($\approx G(OH)=2.7 + G(H)=0.6$). Comparison of $G(-TPB^-)$ loss in the presence of 0.1 or 0.5 M hydroxide (Expts. #10 and #11 in Table 4) with the $G(-TPB^-)$ values in the neutral solutions suggests that O^- is nearly as effective as the OH radical in reacting with TPB^-. The O^- species is predominant relative to OH at pH's above ~12 ($pK(OH \Leftrightarrow O^- + H^+) = 11.9$).[9]

Radiolytic Production of Hydrogen

Radiolytic production of hydrogen was linear with absorbed dose in the range of 0-2 Mrad for all of the 0.05 M TPB^- systems as shown in Figure 2. No hydrogen was detected in any of the blank unirradiated control samples, indicating that hydrogen is not a significant product of thermal TPB^- degradation processes. The precision of the duplicate samples was typically 10 % or better. These results are in agreement with those of Gupta *et al.* in which a constant $G(H_2)$ value of 0.46 molecules/100 eV with dose is reported for radiolysis of aerated 0.05M TPB^- over the dose range of 0-2 Mrad.[11] As in the experiments, their results were determined from irradiating a sealed aqueous 0.05 M TPB^- sample containing ~66 % liquid and ~33 % void-space.[11] Hydrogen production was lowered by ~20 % in the presence of oxygen saturation relative to either the nitrogen-saturated or aerated TPB^- systems (see Expts. #7, #6 and #8, respectively). Hydrogen production appears to be slightly lowered in the alkaline aerated TPB^- systems relative to the neutral aerated TPB^- systems.

Radiolytic Consumption of Oxygen

Changes in oxygen gas concentrations with dose are shown in Figure 3. Radiolytic consumption of oxygen was higher in the oxygen-purged TPB^- system ($G(-O_2) \approx 2.5$, See lower curve in Fig. 3) relative to oxygen consumption from the aerated systems ($G(-O_2) \approx 0.5$-0.7, See upper curves in Fig. 3). These differences in O_2 loss yields could be due to the larger amounts of dissolved oxygen present in the oxygen-purged system ($[O_2]_{gas} \approx 95$ vol % and $[O_2]_{aq} \approx 1\text{x}10^{-3}$ M)[9] relative to the air-purged system ($[O_2]_{gas} \approx 20.8$ vol % and $[O_2]_{aq} \approx 2.4\text{x}10^{-4}$ M).[9] In the oxygen-purged system the rate of loss of oxygen appears to decrease with increasing dose. The reported $G(-O_2)$ value is an average over the total 2 Mrad dose range. In the aerated systems the oxygen loss is fairly constant with dose. The loss of oxygen was calculated from the change in gaseous O_2 with dose relative to ~95 vol % initially present in the sealed oxygenated system and ~20.8 vol % initially present in the sealed aerated system. Oxygen is known to scavenge the precursors of hydrogen, H· and e_{aq}^-, as shown in reactions B1-17 and B1-18 of Table B1 in Appendix B. Such reactions could account for the ~20 % lowered hydrogen yields mentioned above for the oxygenated solutions. Oxygen is also known to be highly reactive with organic radicals, such as the radical species produced from TPB^- shown in reactions B1-26 and B1-29 of Table B1. The data presented in Table 4 for all of the aerated systems (Expts. #8-13) support the previous postulate that oxygen is lost with an assumed $G(-O_2)$ value of ~ -1.0 molecules/100 eV in the sealed aerated 0.05 M TPB^- systems.[11]

Aerated Nitrate/Tetraphenylborate or Nitrite/Tetraphenylborate Solutions

Experiments #12 and #13 in Table 4 show that in the presence of 0.1 M nitrate or 0.1 M nitrite, hydrogen yields from 0.05 M TPB^- were decreased to ≤ 0.31 molecules/100 eV. Suppression of radiolytic hydrogen production by both nitrate[1-3,5] and nitrite[4,5] is well-known and is discussed in detail later in this report.

$G(H_2)$ values of 0.27 and 0.31 for the nitrate and nitrite solutions, respectively, are in good agreement with published $G(H_2)$ data for aqueous solutions containing only the nitrate[1-2] or nitrite[4] ion with no organics present. Plots of the nitrate, nitrite, and TPB^- average concentration versus dose for Expts. #12 and #13 from Table 4 are plotted in Figures 4 and 5, respectively. Although data was collected for only two doses in these systems, the plots of concentration versus dose appear to be linear.

Radiation chemical processes have been extensively studied for aqueous nitrate[1-3,13] and nitrite[4,14-16] systems. Previous radiolysis investigations have also examined the role of organics in the radiation-induced reactions of both nitrate[17-20] and nitrite[17] anions. The nitrate system is discussed below in terms of the observed radiolytic yields and a generalized reaction scheme. Similar discussions are then presented for the nitrite system.

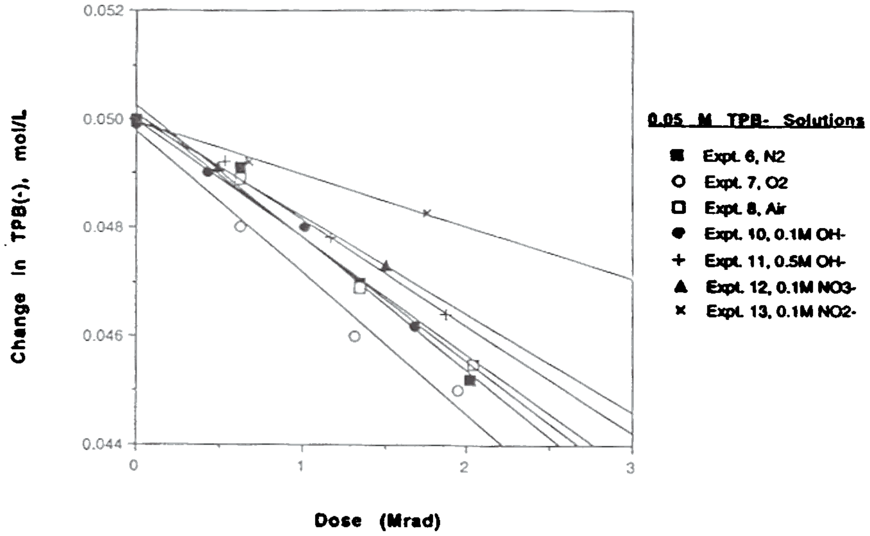


Figure 1. Radiolytic TPB^- decomposition from aqueous 0.05M TPB^- with various solution conditions (See Table 4).

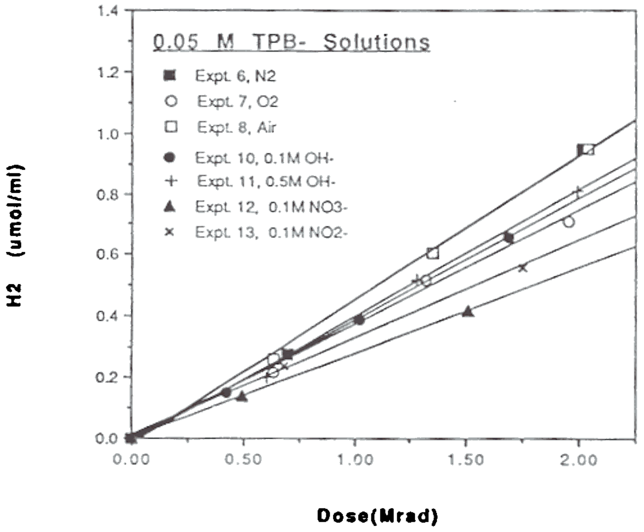


Figure 2. Radiolytic hydrogen production from aqueous 0.05M TPB^- with various solution conditions (See Table 4).

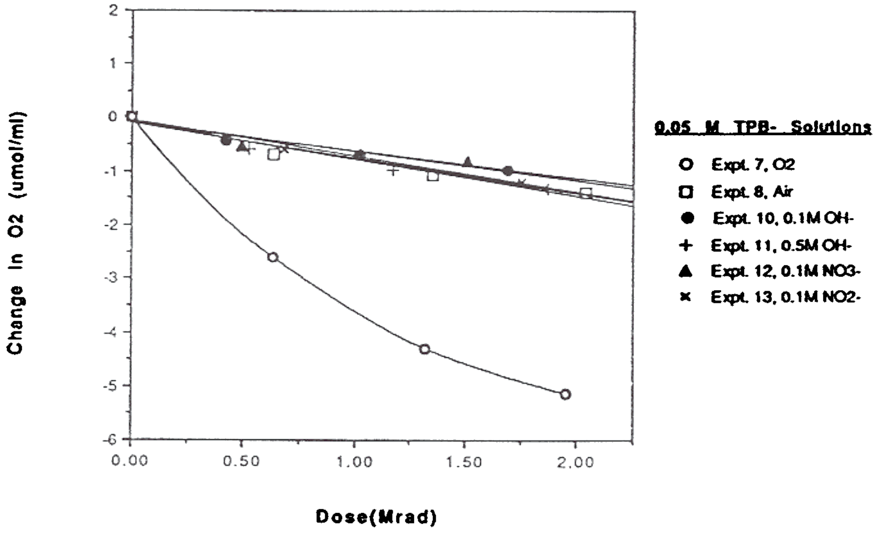
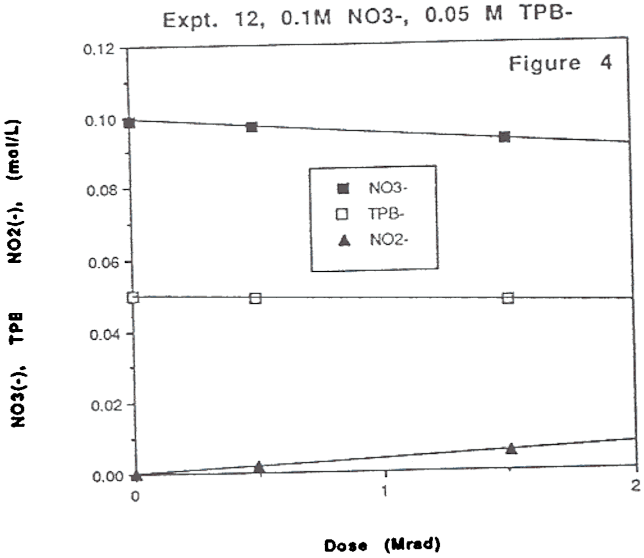
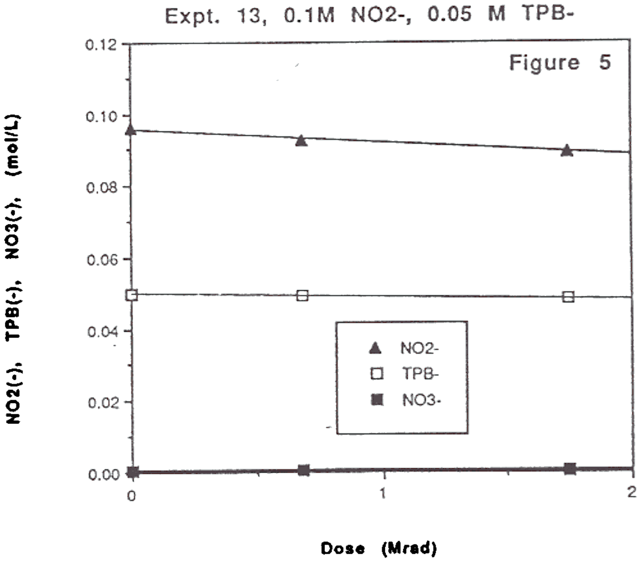


Figure 3. Radiolytic oxygen consumption from aqueous 0.05M TPB^- with various solution conditions (See Table 4).





Figures 4 and 5. Radiolytic yields of nitrate, nitrite and TPB^- from aerated 0.1 M NO_3^- / 0.05M TPB^- solutions (Figure 4); and aerated 0.1 M NO_2^- / 0.05M TPB^- solutions (Figure 5). See Table 4, Expts. #12 and #13, respectively.

Nitrate-Tetraphenylborate Solutions

The radiolysis of aerated 0.01 M nitrate/0.05 M TPB^- solutions (experiment #12 of Table 4) can be generally described by the following reactions. The indicated rates of reaction are reported in references 12 and 21-24.

Primary Reactions: Rate Constants ($M^{-1}s^{-1}$)

1) $NO_3^- + e_{aq}^- \ (+H_2O) \dashrightarrow NO_2 + 2OH^-$ $k = 9.7 \times 10^9 \ (k = 5.5 \times 10^4 s^{-1})$
2) $NO_3^- + H \dashrightarrow NO_2 + OH^-$ $k = 1.4 \times 10^6$

3) $(C_6H_5)_3B(C_6H_5)^- + OH\cdot \dashrightarrow (C_6H_5)_3B(C_6H_5)OH^-\cdot$ $k = 6.2 \times 10^9$
4) $(C_6H_5)_3B(C_6H_5)OH^-\cdot \ (+H_2O)$
$\dashrightarrow (C_6H_5)_3B + C_6H_6OH\cdot + OH^-$

5) $(C_6H_5)_3B(C_6H_5)^- + H. \dashrightarrow (C_6H_5)_3B(C_6H_5)H^-$ $k \approx 1 \times 10^9$ (speculative)
6) $(C_6H_5)_3B(C_6H_5)H^-\cdot \ (+H_2O)$
$\dashrightarrow (C_6H_5)_3B + C_6H_7\cdot + OH^-$

7) $O_2 + e_{aq}^- \dashrightarrow O_2^-$ $k = 1.9 \times 10^{10}$
8) $O_2 + H \dashrightarrow H^+ + O_2^- \ (pK(HO_2 \Leftarrow\Rightarrow H^+ + O_2^-) = 4.88)$ $k = 1.9 \times 10^{10}$

Secondary Reactions

9) $R\cdot + NO_2 \dashrightarrow NO_2^- +$ products
10) $R\cdot + NO_2 \dashrightarrow C_6H_5NO_2 +$ products

11) $R\cdot + NO_2^- \dashrightarrow NO_2^{2-} +$ products
12) $NO_2^{2-} \ (+H_2O) \dashrightarrow NO + 2OH^-$ $(k = 5.8 \times 10^4 s^{-1})$

13) $NO_2 + NO_2 \ (+H_2O) \dashrightarrow 2H^+ + NO_2^- + NO_3^-$ $2k = 9 \times 10^8, \ (k = 1 \times 10^3 s^{-1})$
14) $R\cdot + R\cdot \dashrightarrow$ disproportionation products
or dimer formation

15a) $NO_3^- + HO_2 \dashrightarrow (HO_2NO_3^-) \dashrightarrow OH^- + NO_2 + O_2$
15b) $NO_3^- + O_2^- \dashrightarrow NO_3^{2-} \ (+H_2O) \dashrightarrow NO_2 + 2OH^- + O_2$
16a) $NO_2 + HO_2 \dashrightarrow (HO_2NO_2) \dashrightarrow H^+ + NO_2^- + O_2$ $k = 4 \times 10^9$
16b) $NO_2 + O_2^- \dashrightarrow NO_2^- + O_2$

17) $NO_2 + OH \dashrightarrow (HO_2NO) \dashrightarrow H^+ + NO_3^-$ $k = 1.3 \times 10^9$
18) $NO_2^- + OH \dashrightarrow NO_2 + OH^-$ $k = 1.0 \times 10^{10}$

19) $O_2 + R\cdot$, NO_2 and $NO \dashrightarrow$ products

where $R\cdot$ represents any of the organic radicals $(C_6H_5)_3B(C_6H_5)OH^-\cdot$, $(C_6H_5)_3B(C_6H_5)H^-\cdot$, $C_6H_6OH\cdot$ or C_6H_7

The primary reactions 1-8 above, when considered with their respective rate constants and initial solute concentrations, indicate that the predominant reactions are nitrate with e_{aq}^-, TPB^- with OH, and probably both TPB^- and dissolved O_2 with H. Reaction 3 has been studied by pulse radiolysis.[12] The hydroxyl radical addition to TPB^- forming the $TPBOH^-\cdot$ radical anion was proposed based on comparison of transient spectra for both $TPBOH^-\cdot$ and TPB·. (The tetraphenylboron radical, TPB·, would be formed if TPB^- transferred an electron to OH·) The rate constant for reaction 4 is speculative, based only on comparison to similar (H + aromatic species) rates of reaction.[12] In fact this rate constant could be in the range of 10^4 to 10^9 $M^{-1}s^{-1}$ (see Table 7.7 in **Ref. 9**). Reactions 9-19 are shown as secondary reactions that would involve the products of the primary reactions 1-8, mainly the NO_2 radical produced from reaction 1, any of the organic radicals indicated by R·, and the perhydroxyl radical HO_2 (or its conjugate base O_2^-).

The scheme involving primary and secondary reactions in the aerated nitrate-TPB^- solutions should generally describe the observed radiolytic yields shown for experiment #12 in Table 4. In the 0.1 M NO_3^-/0.05 M TPB^- system comparison of $G(-NO_3^-) = 4.2$ to $G(NO_2^-) = 3.4$ indicates that nitrate is predominately converted via radiolytic reduction processes to nitrite. The observed $G(-NO_3^-)$ yield of 4.2 is very nearly equal to the theoretical yield of $(G(e_{aq}^-) = 3.72 + G(H) = 0.55) = 4.27$ produced in 0.1 M NO_3^- solutions.[25] The calculated hydrated electron yield of 3.72, which is derived from an empirical equation presented in **Ref. 25**, is increased over the hydrated electron yield from dilute solutions $(G(e_{aq}^-=)=2.63)$ due to the high 0.1 M concentration of nitrate present (relative to nitrate ≤ 0.001 M in dilute solutions) and its very fast rate of reaction towards e_{aq}^- as shown in reaction 1 above. Although the hydrogen atom likely reacts predominately with the dissolved $[O_2]_{aq} \approx 2.4 \times 10^{-4}$ M in solution (see reaction 8), the product perhydroxyl radical, or its basic anion O_2^-, could possibly reduce nitrate or NO_2 as shown in reactions 15a,b and 16a,b, respectively.

The observed nitrite yield of 3.4 in these solutions indicates that ~83 % of the original nitrate is reduced to nitrite. This reduction is shown above to occur by reaction 1 followed by reaction 9. Reductions of NO_2 to nitrite, as well as reductions of NO_2^- to NO, by reducing organic radicals are well-established for radicals derived from simple alcohols and formate.[17] Alternative reactions of the organic radicals and NO_2 other than reduction to nitrite, i.e. formation of nitrobenzene, are shown in reaction 10. Nitrobenzene has been identified by liquid chromatographic techniques in the radiolysis of alkaline KTPB slurries in the presence of nitrate and nitrite.[6] It is also possible that some of the nitrite formed from radiolytic reduction of nitrate, could also be further reduced to nitric oxide by the organic radicals as shown in the reaction sequence involving reactions 11 and 12.

The original 0.05 M TPB^- probably serves to scavenge OH radical via the primary reaction 3 above, since nitrate is unreactive with the oxidizing hydroxyl radical. The loss of TPB^-, $(G\text{-}TPB^-) = 1.7$, is lowered somewhat relative to the neutral 0.05 M TPB^- solutions containing no nitrate as shown in Expts. #6-9 in Table 4 $(G(-TPB^-) = 2.2\text{-}2.5)$. It is possible that NO_2 and nitrite produced in the primary reaction 1 and the nitrite produced in secondary reaction 9, both compete with the TPB^- for the OH radical via the secondary reactions 17 and 18, thus lowering the yield for loss of TPB^-.

Nitrite-Tetraphenylborate Solutions

The radiolysis of aerated 0.01 M nitrite/0.05 M TPB^- solutions (experiment #13 of Table 4) can be generally described by the following reactions. The indicated rates of reaction are reported in references **12** and **21-24**.

Primary Reactions: Rate Constants $(M^{-1}s^{-1}$

18) $NO_2^- + OH \text{-->} NO_2 + OH^-$ $k= 1.0 \times 10^{10}$
20) $NO_2^- + e_{aq}^- (+H_2O) \text{-->} NO + 2OH^-$ $k= 4.1 \times 10^9$, $(k=5.8 \times 10^4 s^{-1})$
21) $NO_2^- + H \text{-->} NO + OH^-$ $k= 7.1 \times 10^8$

3) $(C_6H_5)_3B(C_6H_5)^- + OH\cdot \text{-->} (C_6H_5)_3B(C_6H_5)OH^{-}\cdot$ $k= 6.2 \times 10^9$
4) $(C_6H_5)_3B(C_6H_5)OH^{-}\cdot\ (+H_2O)$
$\text{-->} (C_6H_5)_3B + C_6H_6OH\cdot + OH^-$

5) $(C_6H_5)_3B(C_6H_5)^- + H. \text{-->} (C_6H_5)_3B(C_6H_5)H^{-}\cdot$ $k= 1 \times 10^9$ (speculative)
6) $(C_6H_5)_3B(C_6H_5)H^{-}\cdot\ (+H_2O)$
$\text{-->} (C_6H_5)_3B + C_6H_7\cdot + OH^-$

7) $O_2 + e_{aq}^- \text{-->} O_2^-$ $k= 1.9 \times 10^{10}$
8) $O_2 + H \text{-->} H^+ + O_2^-$ $(pK(HO_2 \text{<=>} H^+ + O_2^- = 4.88)$ $k= 1.9 \times 10^{10}$

Secondary Reactions

9) $R\cdot + NO_2 \text{-->} NO_2^-$ + products
10) $R\cdot + NO_2 \text{-->} C_6H_5NO_2$ + products

11) $R\cdot + NO_2^- \text{-->} NO_2^{2-}$ + products
12) $NO_2^{2-} (+H_2O) \text{-->} NO + 2OH^-$ $(k=5.8 \times 10^4 s^{-1}$

13) $NO_2 + NO_2 (+H_2O) \text{-->} 2H^+ + NO_2 + NO_3^-$ $2k= 9 \times 10^8$, $(k=1 \times 10^3 s^{-1})$

14) R + R --> disproportionation products or dimer formation

19) O_2 + R·, NO_2 and NO --> products

22) $NO_2 + NO + H_2O) \rightarrow 2H^+ + 2NO_2^-$ $k = 1.1\times10^9$ $(k=5.3\times10^2 s^{-1})$

23) R + NO --> NO^- + products

24) R + NO --> C_6H_5NO + products

where R· represents any of the organic radicals $(C_6H_5)_3B(C_6H_5)OH^{-}\cdot$, $(C_6H_5)_3B(C_6H_5)H^{-}\cdot$, $C_6H_6OH\cdot$ or C_7H_7:

As shown from the primary reactions 18, 20-21, and 3-8, and their associated rate constants above, it is expected that the original 0.1 M nitrite would readily react with all of the primary radical products from the radiolysis of water. Nitrogen dioxide is the oxidized product formed from OH reaction with nitrite. Nitric oxide is the reduced product formed from either e_{aq}^- or H reaction with nitrite. The 0.05 M TPB^- present could possibly compete with 0.1 M nitrite for the hydroxyl radical. The reactions 9-14, 19 and 22-24 represent secondary reactions of the products of the primary reactions 18, 20-21 and 3-8. These products are expected to be NO_2, NO and the organic radicals R·. Reactions 15a,b and 16a,b from the nitrate/TPB^- scheme have not been included in the nitrite/TPB^- scheme. Reactions 15 and 16 are not included because in the 0.1 M nitrite/0.05 M TPB^- solutions HO_2 would likely be formed to a lesser extent via reaction 8 compared to the 0.1 M nitrate/ 0.05 M TPB^- system, due to the high rate of reaction between (nitrite + H) relative to (nitrate + H), see reactions 21 and 2, respectively. Reaction 17 involving the OH radical oxidation of NO_2 would likely be less significant in the nitrite/TPB^- solutions due to the high rate of reaction for 0.1 M nitrite towards the hydroxyl radical in reaction 18. There is no such analogous reaction between nitrate and the hydroxyl radical in the nitrate/TPB^- reaction scheme.

The above scheme involving primary and secondary reactions in the aerated nitrite-TPB^- solutions should generally describe the observed radiolytic yields shown in Table 4. The nitrite loss of $G(-NO_2^-) = 3.5$ in the 0.1 M NO_2^-/0.05 M TPB^- solutions (experiment #13 in Table 4) does not lead to nitrate formation ($G(NO_3^-)<0.1$), but rather likely to reduced products such as nitroaromatic and nitrosoaromatic organic compounds (i.e. $C_6H_5-NO_2$ and C_6H_5-NO), NO, N_2O and NH_3.

As mentioned earlier, nitrobenzene has been identified by liquid chromatographic techniques in the radiolysis of alkaline KTPB slurries in the presence of nitrate and nitrite.[6] Nitrobenzene and nitrosobenzene are suggested to occur via reactions 10 and 24 above. Although no attempts were made in this study to analyze for NO, N_2O or NH_3, both N_2O and NH_3 have been previously identified in radiolysis studies involving TPB slurries containing nitrate and nitrite.[26] Nitrous oxide is formed from radiation-induced reductive processes involving aqueous solutions of nitric oxide.[27] The suggested reactions are:

25) $NO^- + NO \Leftrightarrow N_2O_2$ $k_{for.} = 1.7\times10^{9}\ M^{-1}s^{-1}$
$k_{rev.} = 6.6\times10^{4}\ s^{-1}$
26) $N_2O_2 + NO \longrightarrow N_3O_3^-$ $k = 3\times10^{6}\ M^{-1}s^{-1}$
27) $N_3O_3 \longrightarrow N_2O + NO_2^-$ $k = 2.35\times10^{2}\ s^{-1}$

Ammonia has been measured as a decomposition product in thermal gas phase reactions of the methyl radical and nitric oxide.[28] The suggested mechanism involves initial formation of the addition complex which rearranges or decomposes to give the oxidized carbon monoxide species and the reduced nitrogen species, i.e. ammonia.

28) $CH_3\cdot + NO \longrightarrow CH_3NO$
29) $CH_3NO \longrightarrow CH_2{=}NOH$
30) $CH_2{=}NOH \longrightarrow CO + NH_3$

Analogous reactions can be postulated to occur in aqueous solutions involving for instance either the tetraphenylborate-hydroxyl radical anion from reaction 3 or the hydroxycyclohexadienyl radical from reaction 4. The product of these postulated reactions would be the dicarbonyl quinone, $C_6H_4O_2$, and ammonia.

31) $(C_6H_5)_3B(C_6H_5)OH^{-}\cdot + NO \longrightarrow (C_6H_5)_3B + (C_6H_5)OHNO^-$
32) $(C_6H_5)OHNO^- \ (+H_2O) \longrightarrow C_6H_4O_2 + OH^- + NH_3$

33) $C_6H_6OH\cdot + NO \longrightarrow C_6H_6OHNO$
34) $C_6H_6OHNO \longrightarrow C_6H_5OHNOH$
35) $C_6H_5OHNOH \longrightarrow C_6H_4O_2 + NH_3$

Similar reactions to that of reaction 32 above, involving hydrolysis of a C=N double bond species to form ammonia, have been suggested to occur with secondary aliphatic amines in aqueous solution.[29] These reactions are:

36) $(CH_3)_2NH \longrightarrow CH_2{=}NH + CH_4$
37) $CH_2{=}NH + H_2O \longrightarrow NH_3 + CH_2O$

Apparently nitrite is effective in protecting the TPB^- from hydroxyl radical attack since $G(-TPB^-) = 0.9$ in the presence of 0.1 M nitrite is lower than the $G(-TPB^-)$ values in the range of 2.2-2.5 for similar 0.05 M TPB^- solutions without nitrite present (see Expts. #6-9 in Table 4). It is likely that nitrate formation is prevented under our experimental conditions due to

1) the secondary reaction 22 involving NO_2 and NO radicals to reform nitrite , and 2) the organic radicals produced in reactions 3-6 that are postulated to subsequently react with NO_2 in reactions 9 and 10. (These three reactions 22, 9 and 10, would prevent the NO_2 disproportionation and hydrolysis reaction 13 from occurring to form nitrate). Organic radical reactions similar to reaction 9 above have been proposed involving reduction of NO_2, as well as nitrite and NO, by the reducing radicals derived from simple alcohols and formate.[17]

Additional Data Pertaining to the Effects of Gas-Purging, Added Hydroxide, Added Nitrate or Nitrite

Additional data pertaining to the 0.05 M TPB^- irradiation Expts. #6-13 shown in Table 4 (production of benzene, 1,4-cyclohexadiene, phenylboric acid, phenol, biphenyl) was also collected and will be reported at a later time. Significant results are briefly summarized below. Concerning the volatile organic gases, we find yields of benzene and 1,4-cyclohexadiene in the ratios of 1:1, 2:1, and 3.5:1 for N_2, air, and O_2-saturated 0.05M TPB^- systems, respectively. These two gases have combined yields in the range of 0.5-0.8 molecules per 100 eV for the neutral 0.05 M TPB^- systems. To our knowledge the detection of 1,4-cylcohexadiene has not been reported in previous TPB^- radiolysis investigations.[6,11-12] The 1,4-cyclohexadiene component was not detected in any of the unirradiated TPB^- systems, i.e. the non-radiation control samples that were initially prepared and later analyzed at the same time as the irradiated samples, indicating that it is indeed a radiation-induced decomposition product. In contrast, benzene was detected in all of the unirradiated TPB^- systems indicating that it is a non-radiolytic or thermal decomposition product of the TPB^-. The 1,4-cyclohexadiene radiolytic yields were negligible when hydroxide, nitrite, or nitrate was present.
The 1,4-cyclohexadiene could possibly result from hydrogen atom reaction with TPB^- (see reactions B1-29 and B1-30b and discussion in Appendix B). This could explain the lack of radiolytic 1,4-cyclohexadiene production in the presence of excess hydroxide, nitrate, or nitrite since all of these components readily react with the hydrogen atom (see the respective reactions B1-15, B1-21 and B1-23 in Table B1 of Appendix B).

Radiolytic Hydrogen Production From Aqueous Solutions Containing Soluble Organics - Theoretical Considerations

The sources of radiolytic hydrogen from aqueous solutions containing soluble organics are the molecular H_2 yield from water itself and hydrogen atom reactions with the dissolved organic molecule.[9] Reactions involving production of hydrogen are shown along with their respective rate constants below.[9,21]

B1-6) $e_{aq}^- + e_{aq}^- \text{-->} H_2 + 2OH^-$ $k = 5.4 \times 10^9\ M^{-1}s^{-1}$
B1-10) $H + H \text{-->} H_2$ $k = 1.3 \times 10^{10}\ M^{-1}s^{-1}$
B1-9) $e_{aq}^- + H \text{-->} H_2 + OH^-$ $k = 2.5 \times 10^{10}\ M^{-1}s^{-1}$

The reactions involving organic molecules and the hydrogen atom formed from water dissociation can be generalized as:[9]

38) RH (aliphatic) + H --> $R\cdot + H_2$, (Hydrogen abstraction forming H_2)
39) RH (aromatic) + H --> $RHH\cdot$ (Hydrogen addition to organic)

Rates of reaction for the above two hydrogen atom reactions with organics are highly dependent on the organic species. These rate constants range from $\sim 1 \times 10^4$ to $\sim 5 \times 10^9\ M^{-1}s^{-1}$.[9] In general aqueous solutions containing aliphatic compounds in excess of ~0.001 M can exhibit $G(H_2)$ values equal to the molecular yield from water dissociation, $G(H_2) = 0.45$, plus the hydrogen atom yield, $G(H) = 0.55$, or a total $G(H_2)$ of ~ 1.0. Such systems involving the aliphatic complexing agents EDTA and HEDTA have recently been investigated by Meisel and co-workers in connection with hydrogen production from Hanford alkaline high-level waste simulants.[30-31] They report $G(H_2)$ values in the range of 0.45 to 0.90 from irradiation of alkaline 0.001 M NO_3^- solutions with the aliphatic organic components present at the respective concentrations of 0.0005 to 0.5 M.[30] In contrast, aqueous solutions containing various amounts of dissolved aromatic compounds (in the concentration range of dilute ~0.001 M through concentrated, saturated aqueous solutions) such as benzene[32], phenol[33], and toluene[34] have reported $G(H_2)$ values equal only to the molecular yield from water, $G(H_2) = 0.45$.

Aqueous Slurries Containing Soluble TPB$^-$ and Solid TPB Salts

Extensive measurements of hydrogen G values have been made during this study using typical waste compositions with various additives present. Although radiolytic hydrogen production has been measured in 0.05 M tetraphenylborate solutions,[11] the present results represent the first measurements of radiolytic hydrogen production from aqueous Na/KTPB slurries.[6,11-12] Table 5 lists the typical higher salt content compositions of different waste types. The ranges of the various salt contents including the lower more dilute compositions of the respective solutions are also given in the notes to Table 5.

Radiolytic Hydrogen Production from Na/KTPB Slurries

The measured G values for hydrogen production from several different aqueous slurries containing soluble TPB$^-$ and solid NaTPB, KTPB or mixed Na/KTPB salts and the experimental conditions are listed in Table 6. Most of the results collected in Table 6 were obtained from radiolysis of ~5-gram samples in sealed 60-mL glass vials over the dose range of 0-50 Mrad. Hydrogen yield versus dose plots for these systems indicated a linear increase in hydrogen with increasing dose over the entire ~50 Mrad dose range. Several of the same slurries were also irradiated in ~40-gram quantities contained in air-sealed 45-mL stainless steel vessels that were connected via ~28 ft of 1/8 inch diameter capillary tubing to pressure transducers outside of the radiation field. These samples were irradiated to a dose of ~20 Mrad. This radiolysis procedure, which allowed for pressure monitoring with dose and post-irradiation total system gas collection under a partial vacuum, has been described in detail previously.[35]

The radiolytic hydrogen production results presented in Table 6 clearly show that as the nitrate and nitrite levels increase, the hydrogen levels decrease. The TPB slurries containing ~1 M NO_3^- plus NO_2^- give average $G(H_2)$ values of 0.09±0.02. For the TPB slurries containing 1.9 M NO_3^- and 0.7 M NO_2^-, the average $G(H_2)$ values are = 0.04 ± 0.01. Slurries containing nitrate-plus nitrite in excess of 3 M have $G(H_2)$ values < 0.03. The one slurry system shown in Table 6 with a relatively high $G(H_2)$ value of 0.34 was determined from irradiating a pre-irradiated, washed slurry that was considerably depleted in both nitrate and nitrite ion concentration relative to the other slurries. The slurry was pre-irradiated to 200 Mrad to simulate storage in the tank farm and washed to simulate the late wash process before treatment of the slurry in the Defense Waste Processing Facility. A detailed analysis of this particular slurry sample can be found in Appendix 1 of Ref. 35.

Radiolytic Hydrogen Production from NaTPB Slurries Containing Minor Additives

Table 7 shows the measured G(H_2) values from irradiation of three different TPB slurries in concentrated salt solutions with various minor component additives present. Details on the preparation of these slurries are in Appendix A. The slurries were made exclusively with sodium salts so any solid TPB present was precipitated as NaTPB. All of the data in Table 7 was obtained from irradiation of duplicate ~10-g slurry samples in sealed 60-mL vials to single doses of ~1.5 Mrad. The slurries were irradiated first without any additives, then with each individual additive present, and lastly with all additives collectively present. The data in Table 7 show that the additives present at the concentration levels shown have no apparent effect on hydrogen production. The slurry data in Table 7 again show that hydrogen production can be correlated with the amount of NO_3^- and NO_2^- present. The nitrate plus nitrite levels increase from the 'high hydroxide' to 'average' to 'high nitrate' slurries. The hydrogen yields respectively decrease from the 'high hydroxide' (G(H_2)≈0.095) to 'average' (G(H_2)≈0.060) to 'high nitrate' (G(H_2)≈0.045).

TABLE 5. Typical Waste Composition Concentrations (molar)

Component	Average[a]	High Nitrate[b]	High Hydroxide[c]
Na^+	5.0	6.0	6.0
NO_3^-	1.9	3.1	1.8
NO_2^-	0.70	0.35	0.52
OH^-	1.5	0.81	3.0
AlO_2^-	0.30	0.20	0.60
SO_4^{2-}	0.13	0.35	0.02
CO_3^{2-}	0.14	0.42	0.02
Cl^-	0.023	0.002	0.002
F^-	0.014	0.001	0.001
PO_4^{3-}	0.009	0.001	0.001
Measured Density (g/mL)	1.232	1.290	1.261

[a] Average waste composition in range of 1.5-5 M Na^+, 0.57-1.9 M NO_3^-, 0.21-0.7 M NO_2^-, and 0.45-1.5 M OH^-.

[b] High Nitrate waste composition in range of 2-6 M Na^+, 1.03-3.1 M NO_3^-, 0.12-0.35 M NO_2^-, and 0.27-0.81 M OH^-.

[c] High Hydroxide waste composition in range of 2-6 M Na^+, 0.59-1.8 M NO_3^-, 0.17-0.52 M NO_2^-, and 1.0-3.0 M OH^-.

TABLE 6. Radiolytic Hydrogen from Irradiation of Slurries

Expt. #	Na^+ (M)	NO_3^- (M)	NO_2^- (M)	Solids (wt %)	Na/KTPB (%)	$G(H_2)$ Value (molecules/100 eV)
	5	1.9	0.7	1.0	100 Na	0.060±.003[a] 0.046±.003
2	5	1.9	0.7	4.9	33 Na/67 K	0.038±.003
3	5	1.9	0.7	5.4	100 Na	0.052±.008[a] 0.030±.003
4	5	1.9	0.7	5.3	100 K	0.028±.004
5	5	1.9	0.7	0	---	0.032
6	5	1.9	0.7	2	100 Na	0.050
7	5	1.9	0.7	5	100 Na	0.042
8	5	1.9	0.7	10	100 Na	0.036
9[b]	0.1	0	0.01	10	100 K	0.34[a]
10	5	1.6	0.53	11	100 K	0.065±.004
11	2	0.6	0.17	6.5	43 Na/57 K	0.11
12	2	0.6	0.17	6.5	43 Na/57 K	0.089±.004[a]
13	2	0.76	0.28	6.7	100 Na	0.074
14	2	1.03	0.12	4.2	17 Na/83 K	0.077
15	6	2.3	0.84	5.4	100 Na	0.028
16	6	3.1	0.35	5.4	33 Na/67 K	0.026

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[a] Hydrogen yields measured by irradiating duplicate 40-45 g samples in air-sealed system consisting of 45-mL steel vessel and ~28 ft of pressure tubing. See Ref. 35 and Appendix A for details. All other hydrogen yield data from irradiation of ~5 g of slurry in sealed 60-mL glass vials.

[b] Slurry pre-irradiated to ~200 Mrad to simulate storage in the tank farm and washed to simulate the late wash process. See Ref. 35 for details.

TABLE 7. Radiolytic Hydrogen from Slurry Waste Compositions with Minor Component Additives

Component	Concentration (molar)		
	Average	High Nitrate	High Hydroxide
NaTPB[a]	0.2	0.2	0.2
Na^+	2.5	6.0	2.0
NO_3^-	0.95	3.1	0.6
NO_2^-	0.35	0.35	0.17
OH^-	0.75	0.81	1.0
AlO_2^-	0.15	0.20	0.20
SO_4^{2-}	0.065	0.35	0.0067
CO_3^{2-}	0.070	0.42	0.0067
Cl^-	0.0115	0.002	0.0007
F^-	0.007	0.001	0.0003
PO_4^{3-}	0.0045	0.001	0.0003

Additives	Concentration (molar)	$G(H_2)$[b] (molecules/100 eV)		
		Average	High Nitrate	High Hydroxide
None[c]	0.0	0.033	0.048	0.094
HCO_2^-	0.017	0.016	0.047	0.092
$NaTi_2O_5H$[d]	(1 wt %)	0.040	0.044	0.087
Sludge[d]	(2 wt %)	0.064	0.043	0.089
Hg^{2+}	0.015	0.058	0.048	0.095
R-OH[e]	0.012	0.064	0.047	0.093
All[f]	-	0.068	0.050	0.098
Average		0.050 (±0.018)	0.047 (±0.003)	0.093 (±0.004)

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[a] Due to the high salt contents, the total 0.2 M TPB was present as both a solid NaTPB precipitate and as dissolved TPB^- ion (typically < 0.02 M) in solution.

[b] Average G values (molecules/100 eV) based on ~1.5 Mrad dose absorbed by duplicate slurry samples. The precision of the results from duplicate samples was typically 10 % or better.

[c] G values determined with no additives present in the simulant slurries.

[d] Titanate and sludge added as solids. Sludge comprised of finely divided particulates containing metal (Fe, Mn, Al, Ni, Zr, Ru, Pd, Rh, Cr, Cu, Mg, Pb, Zn) oxides and hydroxides.

[e] Alcohols added from a stock mixture containing a 5.0 mL:3.2 mL:0.17 mL mixture of 1-butanol, isopropanol, and methanol, respectively.

[f] Slurries contained all additives in the amounts present in the individual additive plus slurry tests.

Aqueous Solutions and Slurries Containing Nitrate and/or Nitrite

During most of the ITP cycle, significant amounts of nitrate, nitrite, and other soluble ions are present in the waste (see Table 5). It is known that the G value for hydrogen production decreases as the concentration of nitrate or nitrite increases in aqueous solutions.[1-5] The lowering of radiolytic hydrogen yields by nitrate and nitrite ions is due to their ability to readily scavenge the precursors, i.e. e_{aq}^- and H, to molecular hydrogen (see reactions B1-20 through B1-23 in Appendix B). Data from previous investigations pertaining to radiolytic hydrogen evolution from deaerated aqueous nitrate[1] or nitrite[4] solutions is shown in Table 8. New measurements of hydrogen yields from ~1 Mrad irradiations of equal-molar mixtures of nitrate plus nitrite solutions are shown in Table 9. These data were obtained from duplicate samples of 10 to 30-mL samples in air-sealed 60-mL vials. Pressure increases from radiolysis were less than +0.5 psig in these tests.

Figure 6 shows the $G(H_2)$ published literature values from Table 8 and results for the nitrate/nitrite solutions from Table 9 plotted against the sum of the nitrate and half of the nitrite concentrations. It has been shown that plotting the $G(H_2)$ values vs. the cubed root of solute concentration yields straight-line fits.[2-3,5] Data from Tables 8 and 9 are also plotted in this manner as shown in Figure 7. Plotting the hydrogen yield data versus the cubed root of concentration produces two distinct linear regions below and above ~1 M nitrate plus one half nitrite concentration. The reason for summing only half of the nitrite concentration for the plots in Figures 6 and 7 is based on the rates of reaction between both the solvated electron and hydrogen atom with nitrate or nitrite. As shown in Table B1, nitrate reacts with e_{aq}^- and H with a combined rate of $9.7\times10^9\ M^{-1}s^{-1}$ (see reactions B1-20 and B1-21), which is ~2X the combined rate of $\sim4.8\times10^9\ M^{-1}s^{-1}$ (see reactions B1-22 and B1-23) for analogous nitrite reactions.

It can be seen from Figures 6 and 7 that treating the nitrate only, the nitrite only, or the nitrate plus nitrite data in this manner produces a very good correlation for $G(H_2)$ vs. either $[NO_3^-] + 1/2[NO_2^-]$ or $([NO_3^-] + 1/2[NO_2^-])^{1/3}$. As mentioned above the reason for plotting the $G(H_2)$ values vs. the cubed root of solute concentration is to derive linear fits to the data that can be readily used in predicting $G(H_2)$ values from nitrate, nitrite, or nitrate-plus-nitrite systems. From Figure 7 linear least square fits of the nitrate and nitrite data over the lower concentration region ($\leq$ 1 M) and over the higher concentration region (> 1 M) yield the following equations.

For $([NO_3^- + 1/2[NO_2^-])$ concentrations up to ~1 M:

$$0 \leq [NO_3^-] + 1/2[NO_2^- \; ^{1/3} \leq 1$$

Equation (#1): $G(H_2) = 0.4597 - 0.3803 * ([NO_3^-] + 1/2[NO_2^-])^{1/3}$

For $([NO_3^-] + 1/2[NO_2^-]$ concentrations in the range of 1-8 M:

$$1 < ([NO_3^- + 1/2[NO_2^- \; ^{1/3} \leq 2$$

Equation (#2): $G(H_2) = 0.1199 - 0.0504 * [NO_3^-] + 1/2[NO_2^-])^{1/3}$

All of the representative $G(H_2)$ values presented in this report (Table 4 for aqueous solutions containing dissolved TPB^- with and without nitrate or nitrite and Tables 6-7 for TPB slurries containing nitrate and nitrite ions) are plotted versus the sum of the nitrate and half of the nitrite concentrations. These plots also contain the published data from Table 8 and results for the nitrate plus nitrite solutions from Table 9. Figure 8 shows the plot of $G(H_2)$ vs. $([NO_3^-] + 1/2[NO_2^-])$ and Figure 9 shows the same data plotted using $([NO_3^-] + 1/2[NO_2^-])^{1/3}$. The hydrogen results from TPB^- solution and TPB slurry irradiations are bounded by the reference data for nitric acid, nitrate, nitrite, and nitrate plus nitrite. Thus equations #1 and #2 presented above are adequate in predicting maximum radiolytic hydrogen yields for the TPB slurries in salt solutions that typically contain both nitrate and nitrite.

An obvious generalization apparent from Figures 8 and 9 is that $G(H_2)$ values appear to be limited to ~0.10 or less if the nitrate plus one half of nitrite concentrations are 1 M or higher, as was the case for most of the slurries irradiated in this study. However as shown earlier in Table 5 the lower range of salt (nitrate plus one half nitrite) concentrations for typical slurries can be ~0.5 M. Figures 8 and 9 suggest an upper limiting value of $G(H_2) \approx 0.20$ for these lower salt-containing TPB slurries. Below 0.5 M (nitrate plus one half nitrite), ion concentration levels would have to be accurately known to predict detailed bounding hydrogen production yields. This is because the change in the hydrogen yields is relatively large, 0.45 to 0.20 molecules per 100 eV, over the 0 to 0.5 M concentration region.

TABLE 8. Literature Values for Radiolytic Hydrogen from Irradiation of Aqueous Solutions Containing Either Nitrate or Nitrite

$G(H_2)$ Value (molecules/100 eV)

Molarity	$NaNO_3$[a]	HNO_3[a]	KNO_2[b]
0.00004	-	-	0.44
0.0012	0.42	0.43	0.41
0.0032	0.39	0.41	-
0.0079	0.39	0.37	-
0.012	-	-	0.36
0.016	-	-	0.35
0.027	0.32	-	-
0.031	-	0.34	-
0.058	-	-	0.32
0.150	0.24	0.25	-
0.165	-	-	0.27
0.310	0.19	0.19	-
0.394	-	-	0.22
0.510	0.15	0.15	-
0.700	0.12	-	-
0.800	-	0.11	-
1.0	0.096	0.091	-
2.0	0.059	0.053	-
3.0	0.045	0.042	-
4.0	0.038	0.035	-
5.0	0.035	-	-
6.0	0.029	0.020	-
7.0	0.025	-	-
8.0	-	0.018	-

---

[a] Data reproduced from Table I of (Mahlman, 1961).[1]

[b] Data reproduced from Table I of (Schwarz, 1955).[4]

TABLE 9. Radiolytic Hydrogen from Irradiation of Aqueous Solutions Containing Both Nitrate and Nitrite

Concentration (molar) NO_3^- (M)	NO_2^- (M)	$G(H_2)$ Value (molecules/100eV)
Low Concentrations[a]		
0.0005	0.0005	0.40±0.01
0.005	0.005	0.38±0.03
0.05	0.05	0.29±0.03
0.25	0.25	0.17±0.01
High Concentrations[b]		
0.5	0.5	0.100±0.010
1.0	1.0	0.052±0.002
1.5	1.5	0.041±0.007
2.0	2.0	0.035±0.007

---

[a] 10-mL duplicate samples irradiated to dose of 1.2 Mrad; The error cited is the (1 σ) standard deviation.

[b] 30-mL duplicate samples irradiated to dose of 0.8 Mrad; The error cited is the (1 σ) standard deviation.

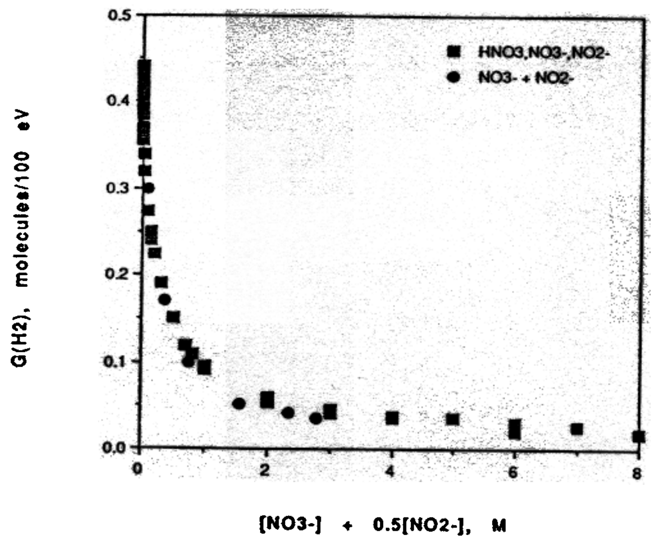

Figure 6. Radiolytic hydrogen production from aqueous solutions containing nitric acid, nitrate, nitrite, or nitrate plus nitrite (See Tables 8 and 9) versus ($[NO_3^-] + 0.5[NO_2^-]$).

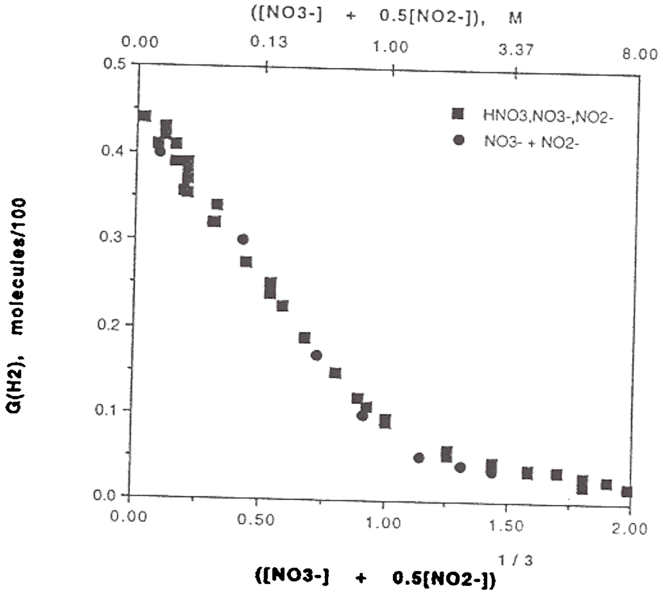

Figure 7. Radiolytic hydrogen production from aqueous solutions containing nitric acid, nitrate, nitrite, or nitrate plus nitrite (See Tables 8 and 9) versus $([NO_3^-] + 0.5[NO_2^-])^{1/3}$.

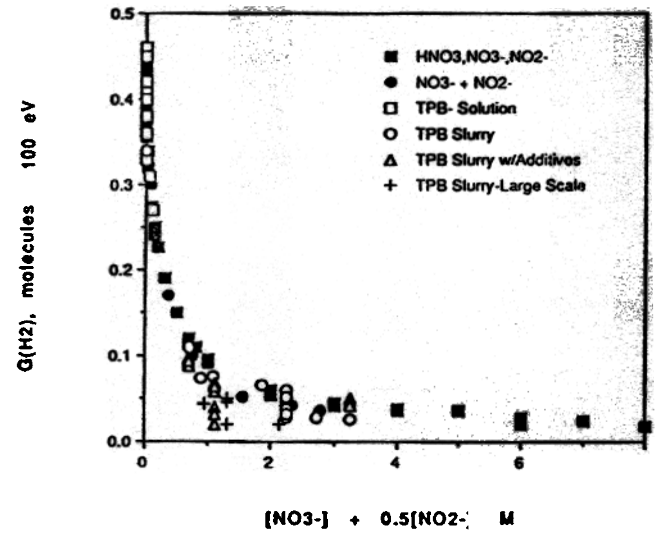

Figure 8 TPB$^-$ solution and TPB slurry hydrogen data and reference nitrate/nitrite hydrogen data plotted versus $([NO_3^-] + 0.5[NO_2^-])$.

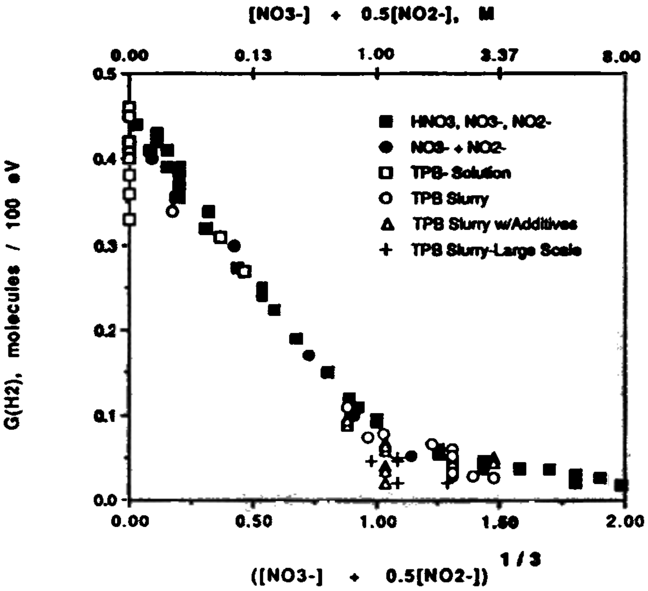

Figure 9. TPB$^-$ solution and TPB slurry hydrogen data and reference nitrate/nitrite hydrogen data plotted versus $([NO_3^-] + 0.5[NO_2^-])^{1/3}$.

CONCLUSIONS

From the data presented in this report it is concluded that:

1. Direct absorption of radiation by TPB solids should not contribute to hydrogen production when TPB slurries in concentrated salt solutions are irradiated. This conclusion is supported by the fact that hydrogen is not detected when small quantities of either NaTPB or KTPB salts are irradiated as air-dried or oven-dried samples and hydrogen is not detected when irradiated NaTPB salts and NaTPB slurry samples are dissolved with water.

2. Radiolysis experiments on aqueous tetraphenylborate solutions involving concentration effects, gas-purging, and added solute effects (OH^-, NO_3^-, and NO_2^-) support the maximum hydrogen yield of $G(H_2) = 0.46$ molecules/100 eV that is presently used in safety calculations.

3. Hydrogen yields from radiolysis of TPB slurries in concentrated salt solutions are significantly lower than hydrogen yields from the TPB^- solution experiments with no salts present. Typical $G(H_2)$ values are < 0.10 molecules/100 eV for the representative TPB slurries irradiated in this study.

4 Decreases in hydrogen production can be correlated with increasing nitrate and nitrite concentrations. Based on numerous experiments presented in this study, the correlation appears to be a valid method of predicting or estimating maximum radiolytic hydrogen production from typical TPB slurries containing known amounts of nitrate and nitrite.

Quality Assurance

Quality assurance of the new data reported here is covered by the following documentation:

Technical Task Request:

HLE-TTR-94106

Technical Task Plan:

D. D. Walker, "Flammable Gas Generation by Radiolysis of Tetraphenylborate Slurries - Technical Task Plan (U)," WSRC-RP-94-1244, November 11, 1994.

Quality Assurance Plan:

D. D. Walker, "Flammable Gas Generation by Radiolysis of Tetraphenylborate Slurries - Quality Assurance Plan (U)," WSRC-RP-94-1251, November 14, 1994.

The data are recorded in Laboratory Notebooks of D. D. Walker (#WSRC-NB-94-257), and C. L. Crawford (#WSRC-NB-93-148, #WSRC-NB-94-326, #WSRC-NB-95-308).

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APPENDIX A

EXPERIMENTAL

Solid TPB Salt Preparation

The sodium tetraphenylborate (NaTPB) used in the dry solids irradiations was purchased from Aldrich Chemical Company and was used without further purification (>99.5 % pure). The KTPB salt was precipitated by adding excess KNO_3 to a concentrated aqueous NaTPB solution prepared with the reagent grade NaTPB. The KTPB solid was filtered and air-dried. No attempts were made to remove any traces of solid NaTPB from the resulting KTPB solids by dissolution with excess rinse water. For measurements of volatile hydrogen from the solid Na or KTPB salts, the solids were irradiated as both air-dried and oven-dried solids (See Table 2). The air-dried samples were prepared under ambient conditions and the oven-dried samples were dried at 105 °C for 12 hrs prior to irradiation. After drying, the oven-dried samples were weighed and allowed to cool to room temperature in a desiccator before they were sealed and irradiated. Pre- and post-drying masses showed that both oven-dried TPB salt forms lost only ~1.5 wt % on drying. All ~1.5 g samples were contained and irradiated in air-sealed 60-mL glass serum vials. Solid reagent-grade NaTPB samples were irradiated in 2-gram quantities in open vessels for both the G(-NaTPB) determinations (See Table 1) and the trapped hydrogen from dissolution of irradiated solid NaTPB solids (See notes to Table 3).

Slurry Preparation

Salt solutions and slurries were prepared from reagent grade chemicals. The chemicals were not further purified before use. The concentrations of several components were verified by analysis by the Analytical Development Section of the Savannah River Technology Center. The NaTPB used in slurry preparation was obtained from Boulder Scientific Co. or from AFF, Inc.- Some the the AFF, Inc., material was spray-dried by Aquafine.

The solids content of KTPB slurries were gravimetrically determined by filtering and washing the KTPB, then drying to constant weight at 105 °C. For NaTPB slurries, the solid NaTPB was dissolved in water, reprecipitated as KTPB, then determined gravimetrically as was done for KTPB slurries.

TPB slurries with additives present were prepared in the following manner. First a small amount of the additive(s) was weighed in a 60-mL glass irradiation vial. To this vial 7.6 mL of the particular salt solution was added. The concentrated salt solutions were made exclusively with sodium salts. The TPB was then added as 2.4 mL of 0.8 M NaTPB aqueous solution. The high salt content of the solution caused some of the dissolved NaTPB to precipitate as NaTPB solids. The resulting mixtures had the salt concentrations shown in Table 5 of the text. When alcohol was used as an additive it was added subsurface to the salt/TPB mixture to minimize any evaporative loss. All the mixtures were briefly air-purged just prior to being sealed and irradiated.

Irradiation Source

All irradiations were made with Co-60 gamma rays using a Co-60 source. The dose rate varied from 2.7×10^5 rad/hr to 1.5×10^5 rad/hr depending on the location of the sample within the source and the month in which the sample was irradiated. Measured temperatures in this source were ~30°C. The source was calibrated with thin film dosimeters containing a radiochromic dye (Far West Technologies, Goleta, CA).[36] The optical density of the film dosimeters was measured on a Hitachi Model 100 UV/VIS spectrophotometer. The thin film dosimetry technique is a secondary standard and was calibrated against the standard Fricke dosimeter.[9,36] The radiation dose to the solid salts, aqueous solutions and slurry samples was calculated based on the dose rate and the time in the source. The radiolytic yields, or G values expressed as the number of molecules produced or consumed per 100 eV of energy absorbed by the system, were calculated based on the number of moles of gas produced (H_2) or consumed (O_2) from irradiation of a known mass of sample.

Several of the simulated TPB slurries shown in Table 6 of the text were also irradiated in an air-sealed system consisting of a 45-mL stainless steel vessel connected via ~28 ft of 1/8 inch diameter capillary tubing to pressure transducers located outside the radiation field. The irradiation procedures, gas collection, and subsequent gas analyses for this system have been described in detail previously.[35] These tests were carried out in a Co-60 source that had a slightly higher dose rate of ~6.9×10^5 rad/hr. The source was calibrated with both an aqueous chemical potassium iodide dosimeter[37-38] and the thin film dosimeters containing a radiochromic dye.[36]

Experimental Procedure

Slurry samples (5-20 g) were sealed in 60-mL glass serum vials. The caps were lined with either thin aluminum foil or polytetrafluoroethylene (PTFE) to prevent loss of hydrogen. Some of the aqueous TPB^- systems were degassed with either oxygen or nitrogen before irradiation (See Table 4). Air was used as the purge gas for the aerated systems. For all of these samples the purging gas was flowed through the liquid via a syringe needle for typically 20 minutes. A venting syringe needle was used during the gas purge to prevent pressure build-up in the sealed 60-mL glass vials. The samples were irradiated in the Co-60 source for a designated period of time to obtain doses in the range of 4 to 50 Mrad for the slurry samples receiving relatively high doses and 0-2 Mrad for the lower dose experiments. The aqueous solution samples were analyzed typically within 12-18 hours after irradiation. After irradiation, the slurry samples were stored in the dark for at least one day but less than one week before analysis.

Analyses for Hydrogen

Hydrogen was analyzed by gas chromatography on a Varian Model 3400 GC using a molecular sieve 13X column (45/60 mesh, 6 ft x 1/8 inch) and a thermal conductivity detector. The instrument was calibrated daily with gas standards purchased from Scott Specialty Gases containing 0.09-10 vol % H_2 in nitrogen. The detection limit was approximately 15 ppm by volume. This limit was determined by making successive dilutions of the least concentrated standard gas (H_2 = 0.09 vol %) and injecting the successive dilutions into the GC until no hydrogen component could be detected. Various amounts of ambient air were mixed with a known volume of the standard gas in a 10-mL gas-tight syringe to produce the diluted samples.

Free or volatile hydrogen was analyzed by removing typically a 2-cc sample of gas from the sealed 60-mL vial using a gas-tight syringe. Typically gas pressures within the vials were measured before any gas analyses. Gas pressures within the vials were found to be small (typically < 1.05 atm) at the higher doses. These small changes in pressures detected in most of the irradiated systems with the organic precipitate present are probably due to the radiolytic production of hydrogen and benzene being offset by the consumption of oxygen. No correction was made for the slight pressurization or for the solubility of hydrogen in the high salt-containing slurry systems. The final gas pressures and calculated amounts of dissolved hydrogen obtained in the aqueous systems shown in Table 4 of the text were included in the G value calculations. The maximum solubility of hydrogen gas in water at 1 atm and ambient temperature is ~0.00078 M.[39] Hydrogen solubility decreases in ionic solutions such as the high salt-containing TPB slurries.[40] Assuming the hydrogen gas in the void space of the sealed vessels was in equilibrium with the liquid phase when sampled, it can be shown that 0.5 % or less of the total hydrogen was dissolved in the slurry solutions. Similar calculations indicate that 3 % or less of the total hydrogen was dissolved in the water of the non salt-containing aqueous solutions shown in Table 4. Typically gaseous H_2 was found to be less than 0.2 vol % in the ~50-mL void space for the slurries sealed in 60-mL vessels shown in Tables 6 and 7, and in the range of 1 to 4 vol % in the ~20-mL void space for the aqueous solutions sealed in 60-mL vessels shown in Table 4.

Gas pressures were estimated using a 0-30 psig pressure gauge fitted with a syringe needle. In separate calibration verification tests the pressure gauge showed excellent linear response with increasing pressure over the range of 0-4 psig. These tests were performed by injecting 5 successive 3-cc volumes of air into sealed, empty 60-mL glass serum vials fitted with the air-tight crimp-top seals. The 0-30 psig pressure gauge also showed linear response over a larger pressure range of 5-20 psig when it was inserted into a gas cylinder regulator gas sampling port, i.e. the pressure gauge readings were in agreement with the gas cylinder regulator pressure readings. The gas cylinder, regulator, and gas sampling port was one of the GC analytical standard gas systems. Pressures less than 1 atm were observed from radiolysis of the O_2-saturated TPB^- solutions, i.e. the pressure indicator of the 0-30 pressure gauge deflected downward below 0 psig when the pressure-gauge syringe needle was inserted into the sealed 60-mL radiolysis vessel after irradiation. This indicated a partial vacuum had occurred over the 2 Mrad dose. These negative pressures were estimated by reading the pressure gauge over the range of 0 to -2.5 psig.

Error Analysis

Errors (±x) are cited in several tables. When applied to experimental measurements, it refers to the 1-sigma standard deviation for results from multiple vials, typically either a triplicate or duplicate set. It captures the random error from preparing vials, irradiation of vials (due to position and elapsed time in source), and benzene or hydrogen analysis. In most cases it does not capture random error from the slurry preparation.

APPENDIX B

RADIATION CHEMISTRY REACTIONS AND HYDROGEN PRODUCTION

Table B1 is a summary of the reactions occurring during the radiolysis of aqueous solutions that are applicable in discussions of radiolytic hydrogen production.[8-10] Reactions involving solutes of importance for this work, i.e. NO_3^-, NO_2^-, $O_2(aq)$, OH^-, and tetraphenylborate ($B(C_6H_5)_4^-$)[6,11-12] are also shown. Rate constants for the reactions are taken from the Buxton *et al.* compilation.[21] The rate constant for OH addition to TPB^- was experimentally determined with pulse radiolysis using competition kinetics.[12] Similar pulse radiolysis experiments established an upper limit for the rate constant involving reaction of e_{aq}^- with TPB^-. The rate constant for H addition to TPB^- is speculative.[12] It was inferred from reaction rates of similar aromatic molecules with the hydrogen atom.[21]

Reactions 1-5 describe the primary events upon radiolysis of water.[10] Reactions 1 and 2 represent direct absorption of radiation by the water molecules indicated by the symbol (VVV->). Reactions 3-5 are very fast chemical reactions of the excited state and ionized water molecules. This scheme is applicable to gamma-ray absorption by water. The events shown in reactions 1-5 take place on a time-scale of $\leq 10^{-12}$ sec after the initial ionizing event, leaving concentrated regions, or spurs, of the primary radicals. Reactions 6-13 describe the reactions of the primary products from water dissociation during the 'spur expansion' which takes place up to about 10^{-7} sec after the initial ionizing event. In the absence of any dissolved solutes, these spur expansion reactions produce a relatively homogeneous distribution of primary radicals and molecular products throughout the bulk aqueous media. The yields of the primary products and molecular products resulting from these reactions are well-documented.[8-10] Reaction 14 occurs along with about six other (molecular product + primary radical) reactions at time-scales of approximately 10^{-7} sec.[10] Reaction 14 is shown here because it is the only such (molecular product + primary radical) reaction that destroys the H_2 formed from reactions 6-13. Reactions 15-16 are of importance since the ITP aqueous slurries all contain OH^- at levels ≥ 0.3 M (See Table 5 of text listing typical TPB slurry compositions).

Reactions 17-18 are applicable when hydrogen yields are measured in open systems in which dissolved oxygen from air ($O_2(aq) \approx 2.5\times10^{-4}$ M) can scavenge the precursors (e_{aq}^-,H) of molecular hydrogen. In aerated aqueous systems containing organic molecules, R, reaction 19 involving oxygen consumption will also occur. The organic radicals, R·, result from attack on the original organic, R, by the primary radicals produced from water dissociation (see for example reactions 26 and 29). Rates of reaction for oxygen plus many organic radicals in aqueous solutions have been collected by Ross and Neta.[24] Such reactions of O_2 with the radicals produced in the TPB^- system (Reactions 26-31) have been previously suggested by Gupta *et al.*.[11]

Reactions 20-25 describe the initial chemistry of both nitrate and nitrite in the radiolysis of aqueous solutions. Both solutes are efficient scavengers of the precursors (e_{aq}^-,H) of molecular hydrogen. If present in appreciable concentration, i.e. typically approaching $1x10^{-4}$ M, solutes such as $O_{2(aq)}$, NO_3^-, NO_2^-, and TPB^- can compete with reactions 6-13 involving the primary radicals. In such cases the solutes are said to 'scavenge' the primary radicals and change the expected yields of molecular products formed in the absence of any dissolved solutes. Scavenging of e_{aq}^- and H by both NO_3^- and NO_2^- reduces the hydrogen yields in aqueous solution. This reduction in hydrogen production is well-correlated with the concentrations of either nitrate or nitrite anions in aqueous systems.[1-5]

Reactions 26-31 are a summary of the radiolysis reactions involving tetraphenylborate. These reactions are taken from schemes presented in the published accounts of TPB^- radiolysis.[6,11-12] We note that reactions 30a-b as shown do not involve production of hydrogen. It has been proposed that the $C_6H_7\cdot$ radical could dimerize producing C_6H_5-C_6H_5 plus $2H_2$ (see reaction 1-11 of **Ref.** 12). However data presented in this report involving aqueous solutions of TPB^- (all $G(H_2)$ values less than or equal to 0.46 molecules/100 eV, see Table 4), as well as previous steady-state radiolysis reports,[32-33,41] and pulse radiolysis reports,[42-44] on aqueous benzene systems does not support hydrogen production by reactions of the $C_6H_7\cdot$ radical. The $C_6H_7\cdot$ radical is formed in aqueous benzene radiolysis by addition of either e_{aq}^- or H to the benzene ring.[41] The work by Studier and Hart involved steady-state radiolysis of benzene in alkaline solutions with measurement of the monomer and dimer products formed. Their results suggest that the $C_6H_7\cdot$ radical reacts ~75 % via reaction 30a and ~25 % via reaction 30b.[41] In fact for the neutral 0.05M TPB^- systems reported in the Table 4 of the present work we have detected using GC instrumentation the products of reaction 30b, i.e. C_6H_6 and C_6H_8. We find yields of benzene and 1,4-cyclohexadiene in the ratios of 1:1, 2:1, and 3.5:1 for N_2, air, and O_2-saturated 0.05M TPB^- systems, respectively. As mentioned earlier in the text this and other data pertaining to these 0.05M TPB^- irradiation experiments (production of benzene, 1,4-cyclohexadiene, phenylboric acid, phenol, biphenyl, loss of parent TPB^-) will be reported at a later time.

TABLE B1. Reactions Involved in Radiolysis of Aqueous Solutions

Water Radiolysis

Primary Events

1) H_2O VVV-> $H_2O^+ + e^-$ (VVV-> indicates direct energy absorption)
2) H_2O VVV-> H_2O^*
3) H_2O^* --> $H + OH$
4) $e^- + nH_2O$ --> e_{aq}^-
5) $H_2O^+ + H_2O$ --> $H_3O^+ + OH$

Reactions During 'Spur Expansion'	**Rate Constant** ($M^{-1}s^{-1}$)
6) $e_{aq}^- + e_{aq}^-$ --> $H_2 + 2OH^-$	k= 5.4 x10^9
7) $e_{aq}^- + OH$ --> OH^-	k= 3.0 x10^{10}
8) $e_{aq}^- + H_3O^+$ --> $H + H_2O$	k= 2.3 x10^{10}
9) $e_{aq}^- + H$ --> $H_2 + OH^-$	k= 2.5 x10^{10}
10) $H + H$ --> H_2	k= 1.3 x10^{10}
11) $OH + OH$ --> H_2O_2	k= 5.3 x10^9
12) $OH + H$ --> H_2O	k= 3.2 x10^{10}
13) $H_3O^+ + OH^-$ --> $2\ H_2O$	k= 1.4 x10^{11}
Reaction of H2 with Primary Radical	
14) $OH + H_2$ --> $H + H_2O$	k= 4.9 x10^8
Reactions for Alkaline Systems	
15) $H + OH^-$ --> e_{aq}^-	k= 2.3 x10^7
16) $OH + OH^-$ <--> $O^- + H_2O$	k(for.)=1.2 x10^{10} k(rev.)=9.3 x10^7
Reactions Involving Dissolved Oxygen	
17) $O_2 + H$ --> HO_2	k= 1.9 x10^{10}
18) $O_2 + e_{aq}^-$ --> O_2^-	k= 1.9 x10^{10}
19) $O_2 + R\cdot$ --> $RO_2\cdot$	k= 1 x10^9
Reactions Involving Nitrate or Nitrite with Primary Radicals	
20) $e_{aq}^- + NO_3^-$ $(+H_2O)$ -->$NO_2 + 2OH^-$	k= 9.7 x10^9
21) $H + NO_3^-$ --> NO_2 + OH-	k= 1.4 x10^6
22) $e_{aq}^- + NO_2^-$ $(+H_2O)$ --> $NO + 2OH^-$	k= 4.1 x10^9
23) $H + NO_2^-$ --> $NO + OH^-$	k= 7.1 x10^8
24) $OH + NO_2^-$ --> $NO_2 + OH^-$	k= 1.0 x10^{10}
25) $O^- + NO_2^-$ $(+H_2O)$ --> $NO_2 + 2OH^-$	k= 3.1 x10^8
Reactions Involving Tetraphenylborate	
26) $B(C_6H_5)_4^- + OH$ $(+H_2O)$--> $B(C_6H_5)_3 + C_6H_6OH\cdot + OH^-$	k= 6.2 x10^9
27a) $2C_6H_6OH\cdot$ --> $C_6H_6 + C_6H_5OH + H_2O$	
27b) --> $C_6H_5\text{-}C_6H_5 + 2H_2O$	
28) $B(C_6H_5)_4^- + e_{aq}^-$ --> products	k< 1 x10^6
29) $B(C_6H_5)_4^- + H$ $(+H_2O)$ --> $B(C_6H_5)_3 + C_6H_7\cdot + OH^-$	k= 1 x10^9
30a) $2C_6H_7\cdot$ --> $C_6H_7\text{-}C_6H_7$	
30b) --> $C_6H_6 + C_6H_8$	
31) $C_6H_6OH\cdot + C_6H_7\cdot$ --> $2C_6H_6 + H_2O$	