

Decomposition of Triphenylborane with Enhanced Comprehensive Catalyst Under Aerated and Inert Conditions

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Enhanced Catalysis Composition Decomposition of Triphenylborane under Aerated and Inert Conditions (U)

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Abstract

This work investigated the decomposition of triphenylborane in a statistically-designed set of tests to determine the effects of four process variables: temperature, hydroxide concentration, catalyst concentration, and atmosphere. Analysis of these tests provide the following conclusions.

- The presence of tetraphenylborate solids facilitate a 10X increase in the rate of decomposition of triphenylborane.
- The presence of oxygen slows the decomposition of triphenylborane.
- The activation energy of the decomposition reaction in the presence of oxygen (59.88 ± 27.73 kJ/mol) is statistically lower than inerted systems (99.11 ± 20.14 kJ/mol).
- Rate constants derived from the nitrogen inerted tests encompass the rate constants from previous tests with slurries. These rate constants agree reasonably with similar values obtained from Tank 48H operations at ambient temperatures.
- For tests conducted in air, the decomposition reaction rate constant correlated with the catalyst concentration. In tests inerted by nitrogen, the same correlation did not hold.

Introduction

The chemistry of the phenylborates in aqueous, alkaline media received intense study as a result of the benzene releases from the In-Tank precipitation (ITP) facility.¹⁻³ Current interest focuses on the tetraphenylborate decomposition intermediates including triphenylborane.

Triphenylborane, quite soluble under these conditions,⁴ reacts rapidly in the presence of catalytic metals. High-Level Waste Engineering requested studies of the decomposition of triphenylborane under simulated waste tank chemistries to ascertain rate-limiting kinetic data.⁵

Crawford and Peterson⁶ originally studied the catalyzed decomposition of the tetraphenylborate intermediates. These studies used copper as the catalyst and provided rate expressions that suggested lower decomposition rates for 3PB than observed in Tank 48H. Hyder⁷ studied the role of oxygen in the decomposition of the intermediates. Hyder's data for 3PB decomposition indicated a possible acceleration of the rate under inert conditions. Therefore, Crawford et al.⁸ studied the decomposition of triphenylborane using copper as the catalyst under inerted conditions and observed a lower rate of decomposition than predicted based on Hyder's data. The highest observed decomposition rate observed for triphenylborane comes from a set of sodium tetraphenylborate decomposition experiments using the Enhanced Comprehensive Catalyst (ECC) in the presence of sodium and potassium tetraphenylborate solids.⁹

This study used a statistically-designed set of experiments to determine the decomposition rates for triphenylborane as a function of ECC concentration, atmosphere (air or nitrogen), temperature, and hydroxide ion concentration. This data will aid in process modeling of the benzene generation in Tanks 48H, 49H and 50H.

Experimental

Researchers studied the decomposition of triphenylborane in sodium hydroxide solutions containing the Enhanced Comprehensive Catalyst (ECC) utilizing a statistical design with the following variables listed in Table 1 and Table 2.

- Table 1. Triphenylborane Decomposition Test Parameters

<u>Parameter</u>	<u>Levels</u>
Temperature	25, 40 and 55 °C
Hydroxide Concentration	0.5, 1.5, and 2.5 M
ECC Concentration	0.5x, 1.0x, and 2.0x
Atmosphere	Air and Nitrogen

Personnel dissolved reagent-grade sodium hydroxide in distilled, deionized water to provide a 0.5 M, 1.5 M and 2.5 M stock solutions. Tests added triphenylborane as the nominally 9 wt % sodium hydroxide adduct obtained from Aldrich Chemical Company.

The tests utilized glass, 160-mL serum vials as the reaction vessel. The vessel contained nominally 75 mL of the sodium hydroxide stock solution along with 3 grams of reagent-grade sodium tetraphenylborate and solid components of the Enhanced Comprehensive Catalyst. The amount of sodium tetraphenylborate provided a 4 wt % potassium tetraphenylborate slurry. The

vessels requiring inert conditioning were sealed and sparged with house-supplied nitrogen for a minimum of 30 minutes. Concurrently, researchers prepared a 1.85 M potassium hydroxide solution by sparging the solution with nitrogen.

Researchers added KOH to each reaction vessel and stirred for approximately 2 - 3 days to allow for potassium precipitation. They then added liquid ECC components to complete the catalyst compositions. The catalyst included the full suite of species including palladium and diphenylmercury as listed in Table 3. Vessels sealed in air according to the matrix were prepared in an identical manner.

Triphenylborane was added following a negative qualitative test performed for the presence of tetraphenylborate ion. A small aliquot of a saturated potassium chloride solution was added to the solution as the qualitative test for tetraphenylborate ion. Personnel removed samples after 30 minutes of stirring at room temperature to provide for the initial intermediate concentrations.

During this experiment, researchers filtered aliquots (~4 mL) of the slurry using a 0.45 micron syringe filter to remove potassium tetraphenylborate solids. Analysis of filtered samples used High Performance Liquid Chromatography (HPLC) with routine quality assurance protocols.¹⁰

Table 2. Statistically Designed Matrix for Triphenylborane ECC-Catalyzed Decomposition

<u>Row</u>	<u>Pattern</u>	<u>Temp</u>	<u>[OH-]</u>	<u>ECC</u>	<u>Atm</u>
1	+++-	55	2.5	High	Air
2	++-+	55	2.5	Low	N ₂
3	+---	55	0.5	Low	Air
4	+--+	55	0.5	High	N ₂
5	-+--	25	2.5	Low	Air
6	++-+	25	2.5	High	N ₂
7	+---	25	0.5	High	Air
8	+--+	25	0.5	Low	N ₂
9	000+	40	1.5	Mid	Air
10	000-	40	1.5	Mid	N ₂
11		40	1.5	None	Air
12		40	1.5	None	N ₂

- Notes: 1. KTPB solids present at 4 wt % concentration.
 2. ECC concentrations represent ratios of High = 2.0X, Mid = 1.0x, and Low = 0.5x.
 3. Temperature in units of °C.
 4. Hydroxide Ion concentration in units of M.
 5. Tests numbered 11 and 12 are control samples, not part of the statistical design.

The experiments occurred at constant temperature. Personnel monitored the temperatures within the air space of the ovens to ± 2 °C using thermometers traceable to NIST standards.

Temperatures were monitored by laboratory and operations personnel at least once per shift.

The laboratory notebook, WSRC-NB-97-61, contains data collected in this investigation. Furthermore, data collected and procedures used in this study met requirements defined in the Task Technical Plan¹¹ and Task Quality Assurance Plan.¹²

Table 3. Enhanced Comprehensive Catalyst

Soluble Metal Additives		Solid Additives	
Cu	1.7 mg/L	MST	2g/L -
Ru	0.8 mg/L	Sludge Solids	2g/L
Rh	0.2 mg/L	Cu	2mg/L
Pd	0.4 mg/L	Ru	4.6 mg/L
Ag	0.6 mg/L	Rh	1.2 mg/L
Fe	2.6 mg/L	Pd	2.2 mg/L
Cr	60 mg/L	Mn	118 mg/L
Hg	2.2 mg/L	Fe	576 mg/L
Cd	0.4 mg/L	Cr	4 mg/L
Zn	8.7 mg/L	Ni	50 mg/L
Mo	12 mg/L	Al	96 mg/L
- Ce	0.3 mg/L	Mg	2 mg/L
Si	16 mg/L	Zn	4 mg/L
Se	1 mg/L	Pb	6 mg/L
As	0.04 mg/L		
Pb	1.2 mg/L	Organic Compounds	
Sn	2.1 mg/L	Diphenylmercury	150 mg/
Co	0.04 mg/L	Benzene	750 mg/L
Ca	12.2 mg/L		
Sr	0.1 mg/L		
La	0.05 mg/L		

HPLC Analysis Difficulties

These samples were prepared for HPLC analysis according to the Task Plan WSRC-TR-96-0364, Rev. 0. This protocol transfers 1.0 mL of sample by pipette into a 10 mL volumetric flask followed by the addition of 2.5 mL of potassium phosphate buffer solution. The analyst then dilutes with acetonitrile to a final volume of 10 mL mark. The mixture in the volumetric flask is

agitated for several minutes and then allowed to stand until separation between the aqueous layer and the acetonitrile layer occurs. The top acetonitrile layer is filtered through a 0.2 micron filter disk and then analyzed by HPLC.

Generally, the compounds (NaTPB, 3PB, 2PB, 1PB, Phenol and biphenyl) prove stable in acetonitrile for at least 24 hours as evidenced by subsequent analysis of the same samples the next day. However, conflicting "time zero" and other irregularities caused the researchers to repeat analysis for several of these samples. In particular, this group of samples, upon standing for a minimum of one hour in acetonitrile, began to noticeably decompose when examined by HPLC. To correct this problem, analysts injected samples onto the HPLC column within 0.5 h of preparation (i.e., before significant decomposition could occur).

Experimental Results

The experiments examined the decomposition of triphenylborane using a statistical design. Tables 4 through 7 and Figures 1 through 4 of Attachment 1 gives the HPLC results for each of the tests performed.

Personnel analyzed the concentrations of the triphenylborane as a function of time to derive pseudo-first order rate constants and determine the confidence of the effect of variables on the rate of decomposition using the Microsoft[®] Excel data regression function.

Effect of Atmosphere

Previous testing does not provide a clear understanding of the effect of atmosphere in the decomposition of triphenylborane. Hyder⁷ showed that oxygen content in the salt solution had a significant affect on the rate of decomposition of the phenylborates. Triphenylborane was examined in three tests. In two of the tests, oxygen was not observed in the solution. These tests showed more decomposition of triphenylborane than the single test which contained oxygen in the solution. Crawford and Peterson⁸ followed with a set of tests under inerted conditions and observed a lower rate of triphenylborane decomposition:

These tests indicate that atmosphere can play a significant role. Tests prepared under a nitrogen atmosphere showed higher pseudo-first order rate constants than samples prepared under air as shown in Table 7 of Attachment 1. The current tests with inerted samples made every effort to maintain the slurry purged with nitrogen along with the headspace of the reaction vessel. Sparging of solutions used in preparing the simulant helped ensure lower concentrations of oxygen in the solutions for the current study. Also, the design of the reaction vessel precluded leaks much better than the equipment used by Crawford.⁸

Comparing the data from test series T5-B1 and T5-C1, as shown in Table 6 of Attachment 1, provides evidence of the role of oxygen. Both series had low levels of catalyst held at 55 °C.

Test series T5-B1 and test series T5-C1 occurred in nitrogen and air, respectively. Test series T5-B1 decomposed readily from 1947 mg/L to 65 mg/L after 68 hours; whereas, test series T5-C1 decomposed from 1715 mg/L to only 1200 mg/L. This represents a reduction in the pseudo-first order rate constants from 0.050 h^{-1} to 0.0053 h^{-1} for series T5-B1 and T5-C1, respectively.

The four test series design as the mid-point to the statistically-designed matrix should show the same effect of atmosphere. These test series include T5-Q and T5-R (of Table 7) along with T5-E1 and T5-F1 (of Table 6) with the former inerted and the latter in air in each series. Comparing test series T5-Q and T5-R shows in a 73 hour period that the air-sealed T5-Q series is slightly more reactive. The T5-Q tests lost 423 mg/L of triphenylborane; whereas, the T5-R series lost 311 mg/L of triphenylborane. Comparing the T5-E1 and T5-F1 test series, the nitrogen-inerted T5-F1 series showed more reaction in which a loss of 407 mg/L versus 358 mg/L for T5-E1. However, due to the slower rate of reaction at $40 \text{ }^\circ\text{C}$ and the problems associated with the analysis of the first set of experiments (as described in the Experimental Section), the data does not confirm the effect of atmosphere on the decomposition of triphenylborane.

Effect of Catalyst Concentration

The effect of catalyst differs for the samples prepared in air or nitrogen. In air atmosphere, the decomposition rate varies with catalyst concentration to the power of 1.5 ± 0.7 . Comparing the T5-A1 and T5-C1 data from Table 6 gives this value. The T5-A1 test in air used a high level of catalyst; whereas, the T5-C1 test, also in air, had a low level of catalyst. The triphenylborane quickly decomposed in the A1 series from 1745 mg/L to 10 mg/L in 26.5 hours. Triphenylborane in the T5-C1 series test decomposed more slowly from 1715 mg/L to only 1200 mg/L after 68 hours.

The regressed data, however, does not show a catalyst concentration dependency in the inerted tests. This indicates sufficient catalyst at the 0.5x level under inert conditions in the presence of tetraphenylborate solids. Examining the data from test series T5-B1 and T5-D1 shows this behavior. Test T5-B1 contained a low level of catalyst, while test T5-D1 had a high level of catalyst. There does not appear to be any difference to the rate of decomposition for the two experiments. Both tests lost approximately 1500-1700 mg/L in the course of 44.5 hours.

Effect of Hydroxide Ion Concentration

We anticipated an increase in the decomposition rate for triphenylborane at higher hydroxide concentration. This effect is not evident by examination of the data. If one compares the decomposition data of test series T5-N and T5-P, the hydroxide ion concentration is 2.5 M and 0.5 M, respectively. Both samples were sealed under nitrogen and were conducted at $55 \text{ }^\circ\text{C}$, and, as stated above, the catalyst concentration difference can be neglected. The pseudo-first order

rate constants derived from the data are 0.06 h^{-1} for test series T5-N and 0.07 h^{-1} for test series T5-P. Likewise, the rate constants derived from the similar test series T5-U and test series T5-X at $25 \text{ }^{\circ}\text{C}$ are 0.003 h^{-1} and 0.002 h^{-1} , respectively.

Temperature Dependence

Table 8 contains pseudo-first order rate constants for the air and nitrogen systems derived from the regressed data. The regression gave activation energies of $59.88 \pm 27.73 \text{ kJ/mol}$ and $99.11 \pm 20.14 \text{ kJ/mol}$ for the air and nitrogen systems, respectively. Figure 5 plots this temperature dependence. Also, Figure 1 includes, for comparison, data previously obtained by Crawford in tetraphenylborate slurries⁹ and copper catalyzed⁸ reactions along with the data from Hyder's⁷ filtrate testing.

The rate constants derived from the data of the nitrogen system provide higher values than the constants from the air system. The data suggests that the slurry of Crawford's study became anoxic. Extrapolation of Crawford's data to lower temperatures shows a faster decomposition at $25 \text{ }^{\circ}\text{C}$ than observed by experiment. The data from the air and inerted experiments indicate that systems with ECC and tetraphenylborate solids prove more reactive than copper-solids or copper-filtrate systems. Additionally, the air system and the inerted system in the current tests bound the Tank 48H data.

Effect of Tetraphenylborate Solid

Previous work¹³ showed the presence of potassium tetraphenylborate or sodium tetraphenylborate solid can increase the rate of decomposition of soluble sodium tetraphenylborate. Scant data exists that examines the role of the solids in the decomposition of triphenylborane; however, the highest rate of decomposition of triphenylborane occurred in a sodium/potassium tetraphenylborate slurry.⁹ Work by other researchers⁸ in exploring the decomposition of triphenylborane in the absence of solid tetraphenylborate exhibited lower rates. This study indicated a rapid decomposition of triphenylborane in a 4 wt % slurry. Hence, the combined data suggests that the presence of precipitate allows decomposition of triphenylborane to accelerate as observed for tetraphenylborate.

Table 8. Pseudo-First Order Rate Constants (h^{-1}) for Triphenylborane

	Air	Nitrogen
55 °C	0.015	0.054
45 °C	0.0077	0.017
25 °C	0.0017	0.0014

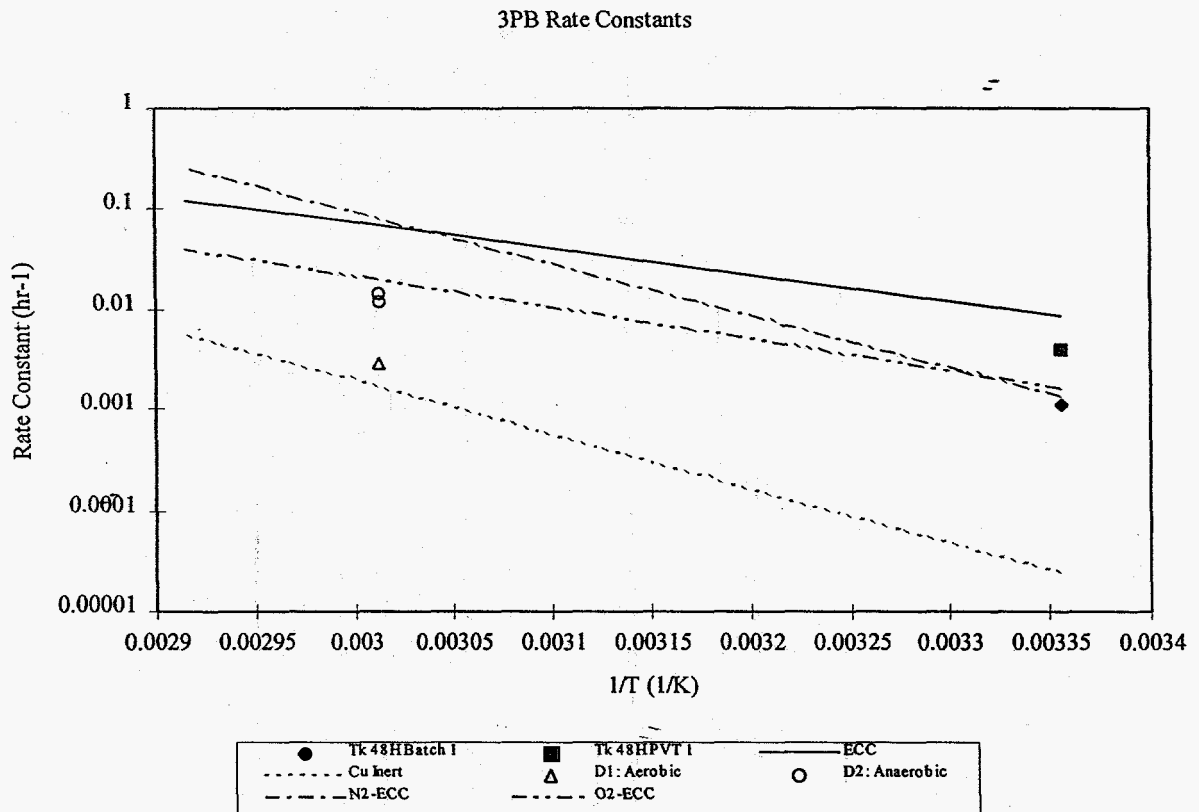


Figure 5. Triphenylborane Decomposition

ECC data are taken from reference 9.

Cu Inert data are taken from reference 8.

N2- and O2-ECC data are from this report.

D1:Aerobic and D2:Anaerobic data are taken from reference 7.

Conclusions

This work studied the decomposition of triphenylborane in a statistically-designed set of tests to determine the effects of four process variables: temperature, hydroxide concentration, catalyst concentration, and atmosphere. The results show two of the process variables are significant: temperature and atmosphere. The catalyst concentration only exhibits a statistically significant influence for triphenylborane decomposition in the presence of air.

The rate constants for the decomposition of triphenylborane in an inerted system exceed those for slurries in air but also show a higher activation energy. In the presence of air, the data suggests a lower activation energy with the rate constants at 25 °C overlapping the inerted system values. The actual role of oxygen in this system is not completely understood. For either system, the observed rate constants bound values estimated from Batch 1 in Tank 48H, but not PVT-1, and exceed values for copper catalysis or ECC catalysis in filtrates by approximately one order of magnitude.

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Attachment 1. Analytical Results from ECC-Catalyzed Decomposition of Triphenylborane.

Table 4. Analytical Results from the 55 °C Tests

Sample	Reaction Time (h)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Temp (°C)	[OH]	Atm	[Catalyst]
T5-M-0	0	1458	193	151	453	55	2.5	Air	High
T5-M-1	64.5	10	25	551	488	55	2.5	Air	High
T5-M-2	95.5	10	12	417	518	55	2.5	Air	High
T5-N-0	0	1340	159	126	410	55	2.5	N ₂	Low
T5-N-1	64.5	32	469	510	453	55	2.5	N ₂	Low
T5-N-2	95.5	10	320	598	463	55	2.5	N ₂	Low
T5-O-0	0	1325	259	176	460	55	0.5	Air	Low
T5-O-1	64.5	480	284	473	483	55	0.5	Air	Low
T5-O-2	95.5	368	260	454	528	55	0.5	Air	Low
T5-O-3	137.5	241	221	452	583	55	0.5	Air	Low
T5-P-0	0	1049	383	262	517	55	0.5	N ₂	High
T5-P-1	64.5	10	34	784	432	55	0.5	N ₂	High
T5-P-2	95.5	10	34	730	437	55	0.5	N ₂	High

Table 5. Analytical Results from the 25 °C Tests

Sample	Reaction Time (h)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Temp (°C)	[OH]	Atm	[Catalyst]
T5-U-0	0	1416	161	133	409	25	2.5	Air	Low
T5-U-1	64.5	1379	183	130	413	25	2.5	Air	Low
T5-U-2	95.5	1312	188	128	394	25	2.5	Air	Low
T5-U-3	137.5	1162	216	149	377	25	2.5	Air	Low
T5-V-0	0	1241	176	149	409	25	2.5	N ₂	High
T5-V-1	64.5	1128	213	139	397	25	2.5	N ₂	High
T5-V-3	137.5	834	281	170	429	25	2.5	N ₂	High
T5-W-1	64.5	949	391	205	445	25	0.5	Air	High
T5-W-2	95.5	923	357	225	444	25	0.5	Air	High
T5-W-3	137.5	439	589	305	549	25	0.5	Air	High
T5-X-0	0	1327	226	166	453	25	0.5	N ₂	Low
T5-X-1	64.5	1216	259	173	425	25	0.5	N ₂	Low
T5-X-3	137.5	1068	271	184	440	25	0.5	N ₂	Low

Table 6. Analytical Results from the 40 °C Tests

Sample	Reaction Time (h)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Temp (°C)	[OH]	Atm	[Catalyst]
T5-Q-1	64.5	1048	303	237	447	40	1.5	Air	Mid
T5-Q-2	95.5	893	338	219	478	40	1.5	Air	Mid
T5-Q-3	137.5	625	351	269	476	40	1.5	Air	Mid
T5-R-1	64.5	405	258	500	450	40	1.5	N ₂	Mid
T5-R-2	95.5	322	269	554	455	40	1.5	N ₂	Mid
T5-R-3	137.5	94	264	587	459	40	1.5	N ₂	Mid
T5-S-0	0	1525	184	119	382	40	1.5	Air	None
T5-S-1	64.5	1498	184	124	374	40	1.5	Air	None
T5-S-2	95.5	1576	221	128	402	40	1.5	Air	None
T5-S-3	137.5	1381	138	104	388	40	1.5	Air	None
T5-T-0	0	1410	172	128	364	40	1.5	Air	None
T5-T-2	95.5	1648	199	132	397	40	1.5	Air	None
T5-T-3	137.5	1442	143	111	370	40	1.5	Air	None
T5-STD-1	64.5	1502	168	130	396	40	1.5	Air	None
T5-STD-3	137.5	1581	39	27	78	40	1.5	Air	None

Note: T5-STD-1 and -3 are standards used for quality control.

Table 6. Analytical Results from Additional Tests at 55 °C

Sample	Reaction Time (h)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Temp (°C)	[OH]	Atm	[Catalyst]
T5-A1-0	0	1745	107	80	189	55	2.5	Air	High
T5-A1-1	18	270	416	612	130	55	2.5	Air	High
T5-A1-2	26.5	10	193	858	164	55	2.5	Air	High
T5-A1-3	44.5	10	58	763	210	55	2.5	Air	High
T5-A1-4	51.5	10	46	667	232	55	2.5	Air	High
T5-A1-5	68	10	27	589	278	55	2.5	Air	High
T5-B1-0	0	1947	58	50	148	55	2.5	N ₂	Low
T5-B2-1	18	752	710	250	107	55	2.5	N ₂	Low
T5-B2-2	26.5	503	874	265	113	55	2.5	N ₂	Low
T5-B1-3	44.5	203	957	346	117	55	2.5	N ₂	Low
T5-B1-4	51.5	156	993	376	113	55	2.5	N ₂	Low
T5-B1-5	68	65	934	467	113	55	2.5	N ₂	Low
T5-C1-0	0	1715	348	96	230	55	0.5	Air	Low
T5-C1-1	18	1650	423	220	183	55	0.5	Air	Low
T5-C1-2	26.5	1605	435	137	154	55	0.5	Air	Low
T5-C1-3	44.5	1335	491	200	152	55	0.5	Air	Low
T5-C1-4	51.5	1249	541	224	166	55	0.5	Air	Low
T5-C1-5	68	1200	511	266	181	55	0.5	Air	Low
T5-D1-0	0	1529	348	96	144	55	0.5	N ₂	High
T5-D1-1	18	339	999	403	113	55	0.5	N ₂	High
T5-D1-2	26.5	66	910	566	145	55	0.5	N ₂	High
T5-D1-3	44.5	9	416	863	155	55	0.5	N ₂	High
T5-D1-4	51.5	10	344	888	153	55	0.5	N ₂	High
T5-D1-5	68	10	170	934	164	55	0.5	N ₂	High

Table 7. Analytical Results from Additional Tests at 40 °C

Sample	Reaction Time (h)	3PB (mg/L)	2PB (mg/L)	1PB (mg/L)	Phenol (mg/L)	Temp (°C)	[OH]	Atm	[Catalyst]
T5-E1-0	0	1692	117	70	195	40	1.5	Air	Mid
T5-E1-1	18	1677	202	103	133	40	1.5	Air	Mid
T5-E1-2	26.5	1746	203	76	125	40	1.5	Air	Mid
T5-E1-3	44.5	1548	320	104	188	40	1.5	Air	Mid
T5-E1-4	51.5	1387	358	115	143	40	1.5	Air	Mid
T5-E1-5	68	1334	400	127	146	40	1.5	Air	Mid
T5-F1-0	0	1813	123	123	141	40	1.5	N ₂	Mid
T5-F1-1	18	1591	251	124	166	40	1.5	N ₂	Mid
T5-F1-2	26.5	1534	280	98	144	40	1.5	N ₂	Mid
T5-F1-3	44.5	1614	299	89	83	40	1.5	N ₂	Mid
T5-F1-4	51.5	1467	328	100	125	40	1.5	N ₂	Mid
T5-F1-5	68	1406	373	119	121	40	1.5	N ₂	Mid

Figure 1. 3PB Decomposition at 55 °C

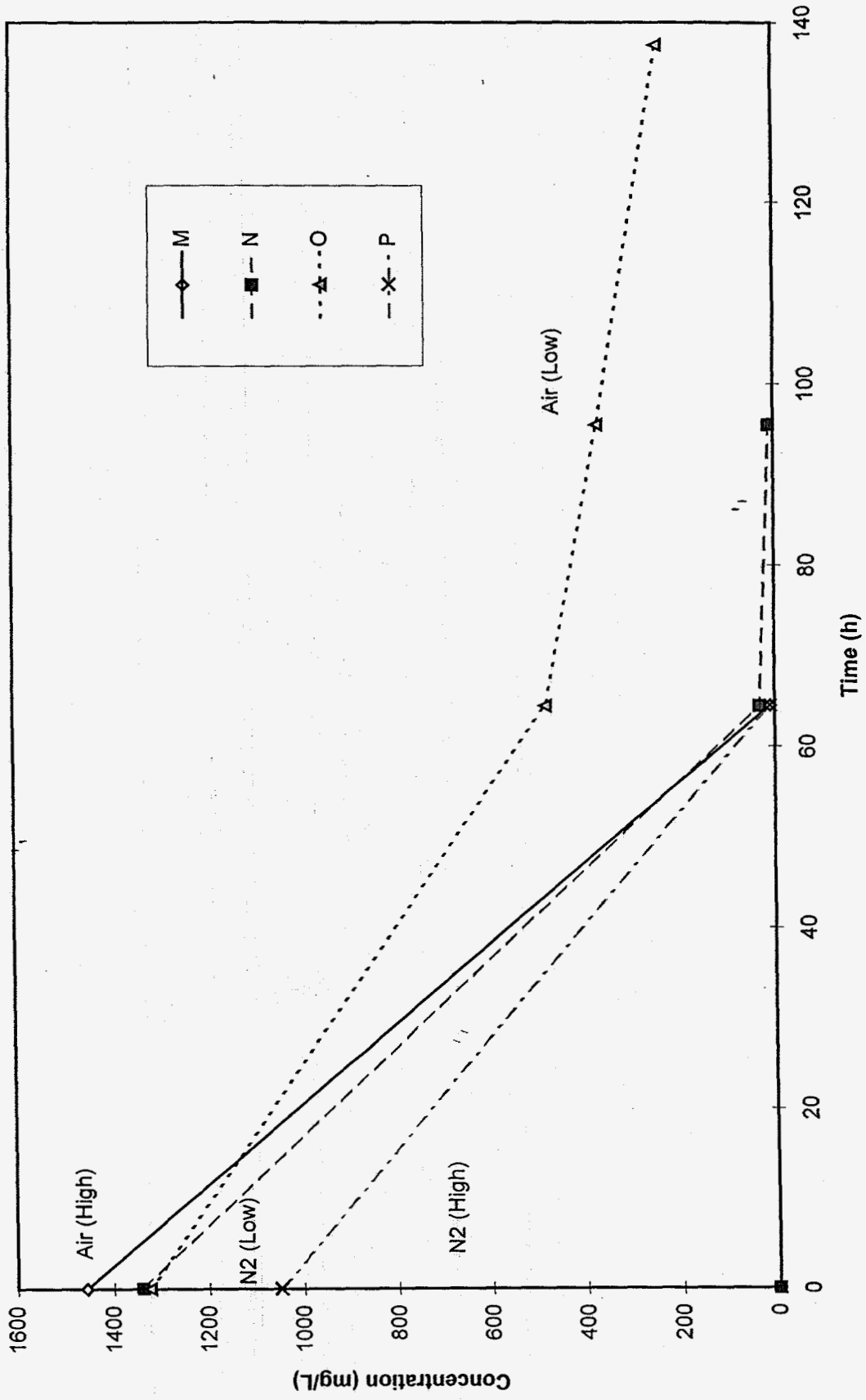


Figure 2. 3PB Decomposition -Additional Tests

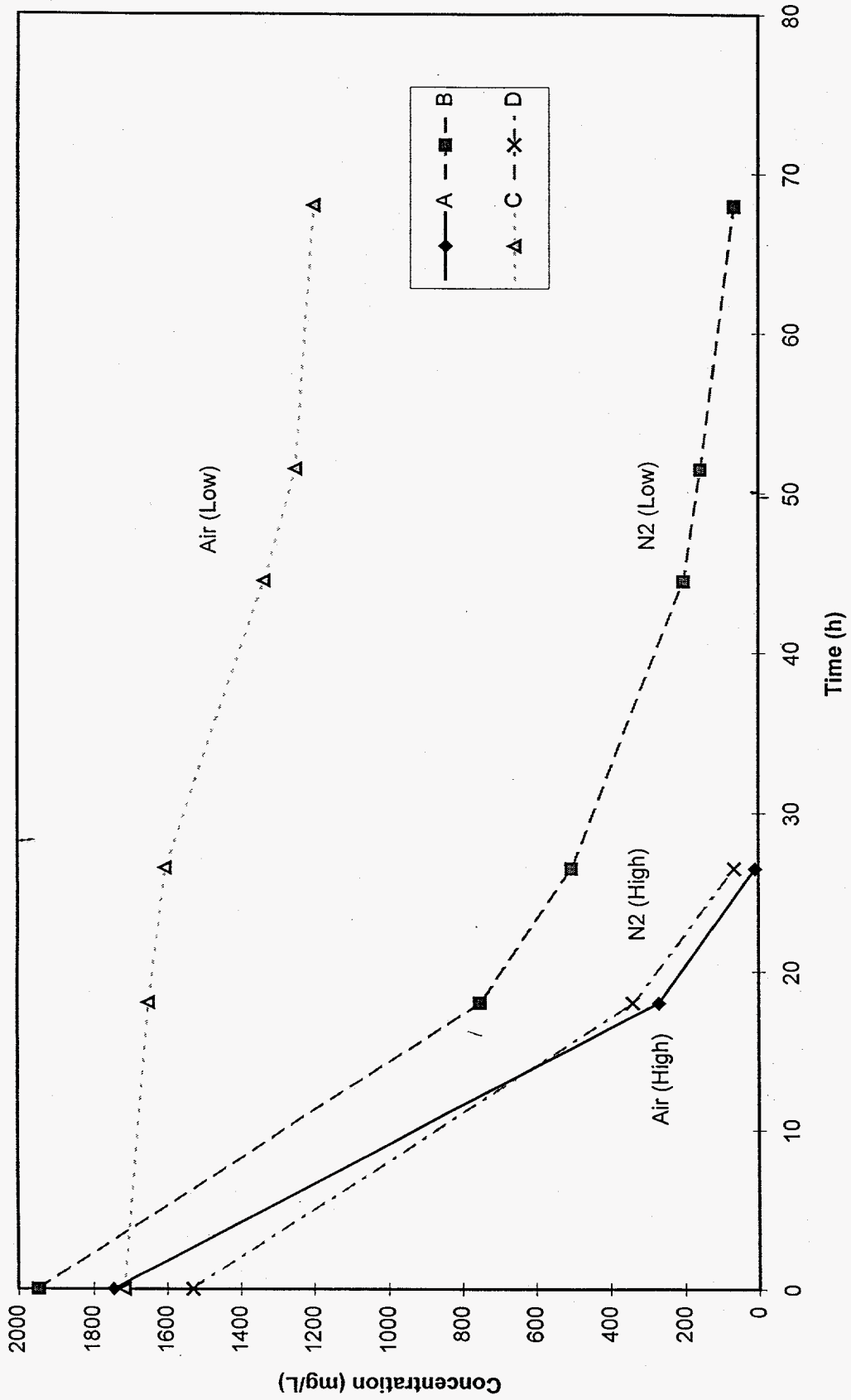


Figure 3. 3PB Decomposition at 25 °C

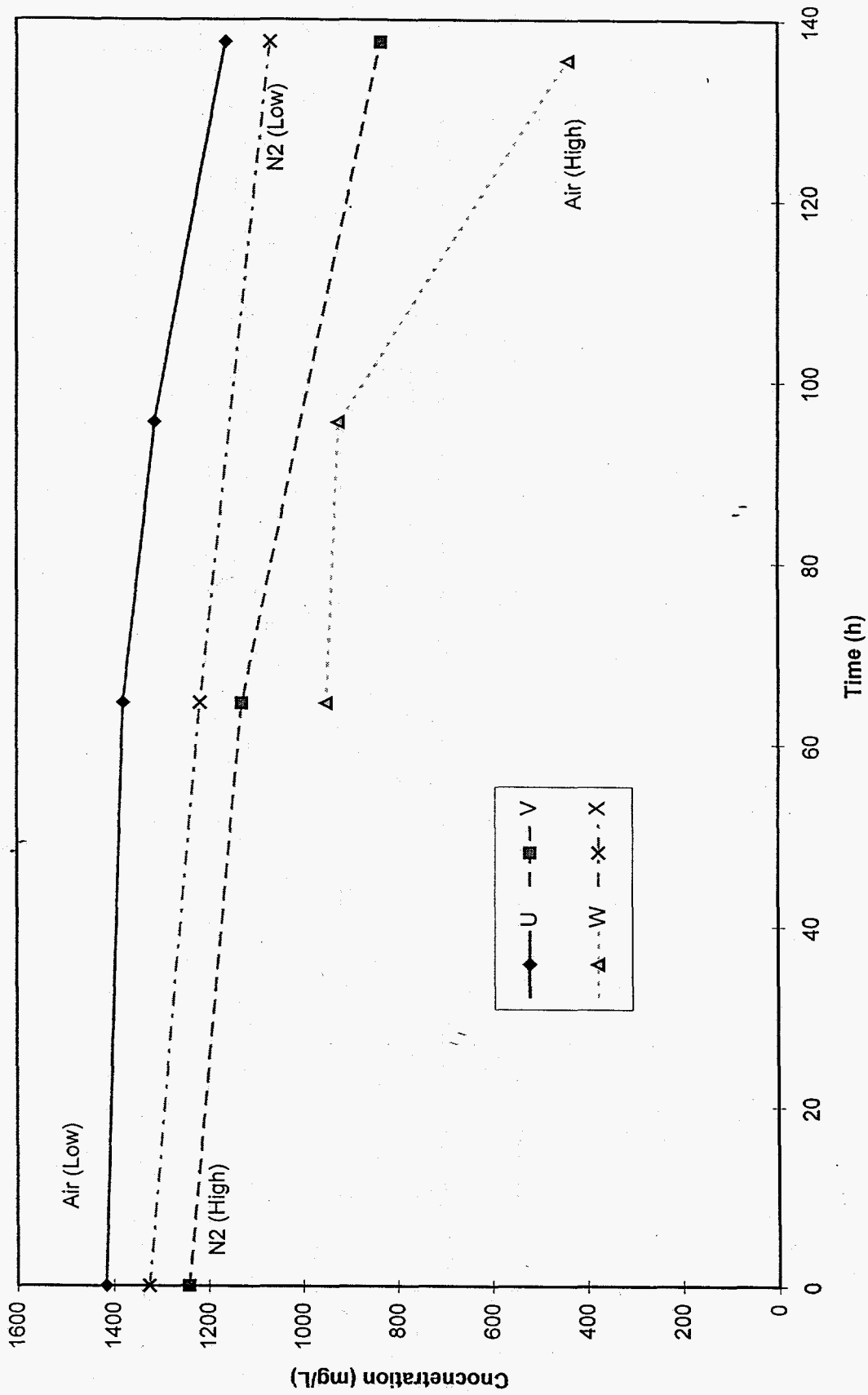
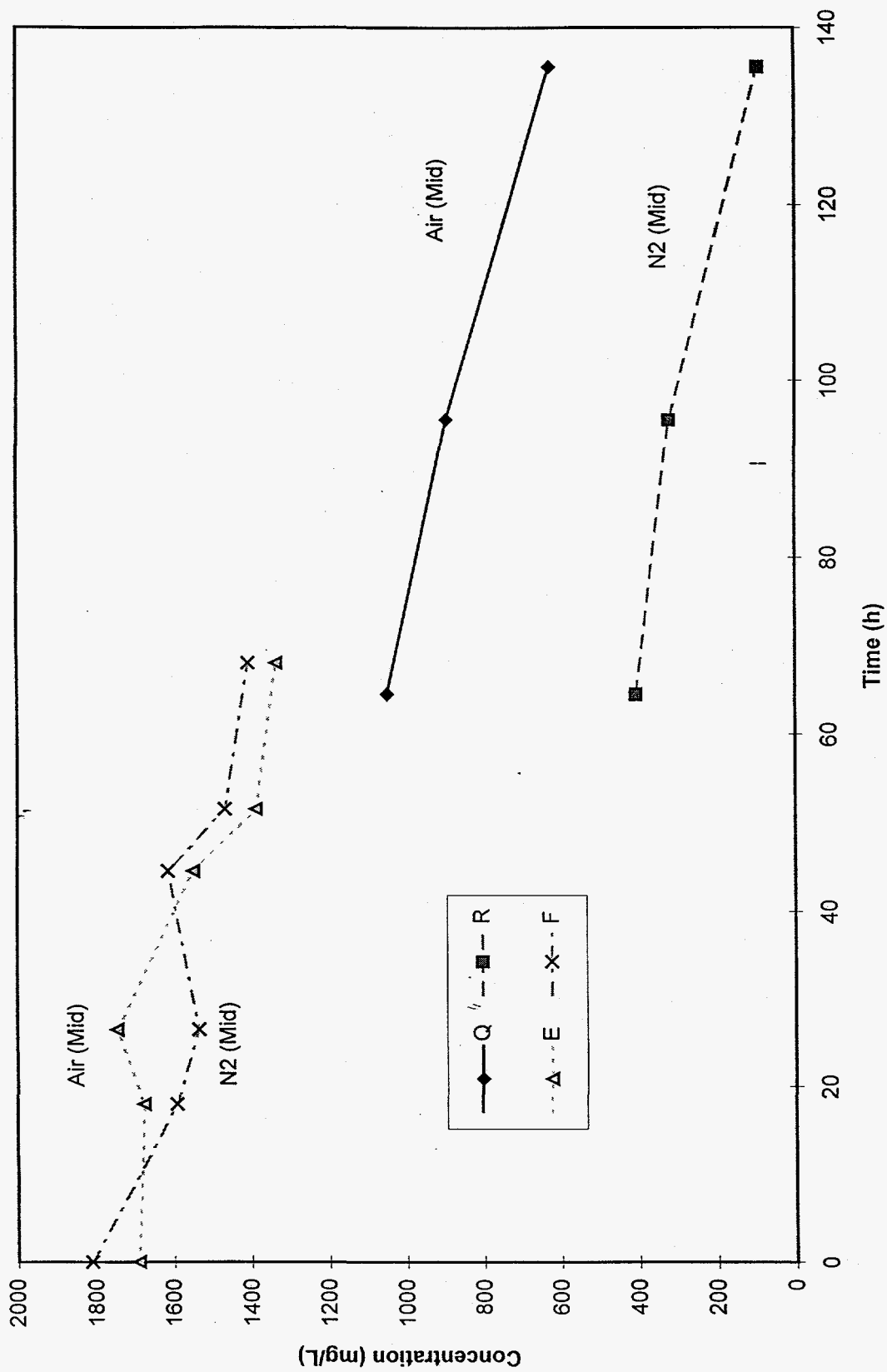



Figure 4. 3PB decomposition at 40 °C

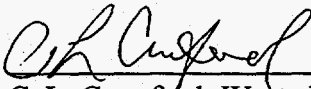


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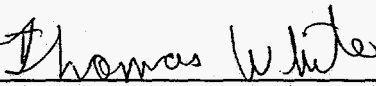
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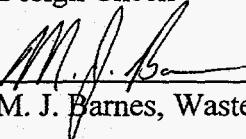


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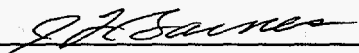
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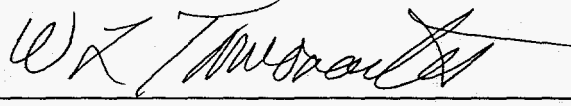
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