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RESEARCH ON HYDRAZINE DECOMPOSITION

27

Fifth Quarterly Progress Report

A. E. Axworthy
J. M. Sullivan
A. Passchier
S. Cohz
E. Welz

July 1968

Rocketdyne
A Division of North American Rockwell Corporation
Canoga Park, California

TECHNICAL REPORT AFRPL-TR-68-138

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Air Force Rocket Propulsion Laboratory
Research and Technology Division
Edwards Air Force Base, California
Air Force Systems Command
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FOREWORD

The research reported herein was supported by the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Edwards Air Force Base, California, Air Force Systems Command, United States Air Force, under Contract F04611-67-C-0087, with Mr. A. Beale serving as Project Monitor.

The work described covers the period 1 April 1968 through 30 June 1968. The Responsible Scientist for the program is Dr. A. E. Axworthy, Principal Scientist of Physical Chemistry. The Program Manager is Dr. K. H. Mueller, Manager of Physical Chemistry and Propellant Technology. The work was conducted by members of Physical Chemistry, supervised by Dr. Axworthy; Analytical Chemistry, supervised by Dr. V. H. Dayan; and SSFL Analytical Chemistry, supervised by Miss N. Sutton. The principal contributors to the program were Dr. Axworthy, Mr. J. M. Sullivan, Dr. A. Passchier, Mr. S. Cohz, and Mr. E. Welz.

This report has been assigned the Rocketdyne report No. R-7146-5.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. EBELKE, Colonel, USAF
Chief, Propellant Division

ABSTRACT

The kinetics of the decomposition of liquid hydrazine was investigated in sealed ampoules. The effects of temperature, hydrazine purity, additives, and type of metal surface present were studied.

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SUMMARY

Hydrazine purified at AFRPL was found to have the same stability at 171 C as the sample which had been purified by Olin Mathieson Chemical Corporation by a different method. The RPL purified hydrazine decomposed only 0.45 percent during 13 hours at 275 C (527 F) in quartz ampoules.

Prepassivation of the pyrex ampoules was found to decrease the decomposition rate of propellant-grade hydrazine at 128 C. It was established that the observed decomposition of propellant-grade hydrazine at 128 C occurs in the liquid phase.

Solvent studies were conducted at 171 C with both purified and propellant-grade hydrazines at concentrations from 20 to 100 percent in aniline. The apparent reaction order was about 2/3 in each case, indicating that the decomposition rate is not a strong function of both the dielectric constant and the hydrazine concentration.

The pretreatment of 347 stainless steel with hydrazine at room temperature decreases its activity toward hydrazine decomposition (at 128 C) by more than a factor of 2. After being in contact with decomposing hydrazine at 128 C for 64 hours, the activity of the surface of 347 stainless steel is reduced by an additional factor of 4. The relative reactivities of individual metal specimens do not remain in the same ratios before and after the latter passivation process. Experiments conducted with passivated metal surfaces indicated the following order of catalytic activity: 321 stainless steel < Al < 304 stainless steel < Cu < Chromel A < 316 stainless steel < Fe, Ni.

The addition of 1 weight percent carbazic acid to purified hydrazine increases the decomposition rate in pyrex at 171 C by a factor of 6. The stoichiometry was the same in the presence of added carbazic acid as with the neat purified hydrazine in the passivated ampoules (5.5-percent ammonia decomposed). The addition of 1 percent carbazic acid to hydrazine is equivalent to reacting the hydrazine with 0.58-percent CO_2. A mechanism involving the $N_2H_5^+$ ion as an intermediate is suggested by the results obtained with added carbazic acid, water, and NH_4Cl.

Several samples of hydrazine were analyzed for carbazic acid and other impurities. Development of the carbazic acid analysis method was not completed, but the results indicate that about 0.1-percent carbazic acid may be present in propellant-grade hydrazine.

These experiments show that the decomposition of hydrazine is strongly acid catalyzed. This phenomenon is most clearly evident in the presence of metal surfaces. The addition of 1 weight percent NH_4Cl in the presence of 321 stainless-steel surfaces increased the percentage decomposition during 3 hours at 128 C by a factor of 10^3.

The addition of 7.8-percent NH_3 to propellant-grade hydrazine did not affect its decomposition rate at 171 C.

INTRODUCTION

It is the objective of this program to establish the stability of liquid hydrazine under various conditions and to elucidate the decomposition mechanisms involved. The role of impurities in the decomposition is being determined. It is anticipated that the decomposition mechanisms in the highly polar liquid hydrazine will differ from those of the vapor-phase reaction.

The program is divided into three tasks: Task I: Decomposition in Glass Reactors, Task II: Heterogeneous Decomposition on Metal Surfaces, and Task III: Role of Impurities.

It was found previously on the program (Ref. 1 through 4) that propellant-grade hydrazine decomposes slowly in pyrex ampoules at the highest temperature studied (211 C) and that the decomposition rate decreases with time. The decomposition occurs mainly in the liquid phase at 171 C (rather than on the reactor wall or in the vapor phase). Propellant-grade hydrazines in use at Rocketdyne and at the Air Force Rocket Propulsion Laboratory decomposes at similar rates.

The rate of decomposition of a hydrazine specially purified by Olin Mathieson Chemical Corporation was found to be smaller than that of propellant grade by approximately an order of magnitude at 171 C. The purified hydrazine decomposes heterogeneously on the pyrex wall.

It was found also that the rate of decomposition of liquid propellant-grade hydrazine on metal surfaces varies by a factor of 200, depending on the type of metal. The decomposition rates on the metal surfaces are not as reproducible as those obtained in the absence of metal. The calculated activation energies for propellant-grade hydrazine on 347 stainless steel and on 321 stainless steel are 20 and 25 kcal/mole, respectively.

Of the known impurities present in propellant-grade hydrazine, only water caused an appreciable increase in decomposition rate when added to the purified hydrazine. However, the addition of as much as 2-percent water did not increase the rate to that obtained with propellant-grade hydrazine. It is apparent, therefore, that another (as yet unidentified) impurity is present in propellant-grade hydrazine.

Experiments were conducted during this report period under each of the three tasks.

TASK I: DECOMPOSITION IN GLASS REACTORS

The study of the decomposition of liquid hydrazine in glass ampoules at elevated temperatures was continued. The goal of this task is to determine the inherent thermal stability of liquid hydrazine and to determine the mechanisms of the homogeneous liquid-phase decompositions of purified and propellant-grade hydrazine. Both pyrex and quartz ampoules were employed during this report period.

RESULTS AND DISCUSSION

Purified Hydrazine

It was established previously on this program that hydrazine specially purified by Olin Mathieson Chemical Corporation (by fractional crystallization) is much more thermally stable than propellant-grade hydrazine. Hydrazine recently purified at AFRPL (by distillation) was tested under similar conditions (171 C, 3 mm ID pyrex ampoules). The amounts decomposed in triplicate 20-hour runs were 0.19, 0.18, and 0.13 percent and, in 40-hour runs, 0.31, 0.28, and 0.24 percent. These decomposition rates at 171 C are about the same as those obtained with the Olin Mathieson Chemical Corporation material (Fig. 1, Ref. 3).

Quartz ampoules were employed in some experiments at higher temperatures because it is less likely that strains will develop during the sealing process. This should reduce ampoule breakage at the higher vapor pressures. The Olin Mathieson Chemical Corporation purified hydrazine was tested at 210 C in 2 mm ID quartz ampoules. The results obtained at 4, 15, 23, 41, 53, and 69 hours gave an approximately linear decomposition rate of 0.060 percent per hour. This rate in quartz ampoules is about the same (see table below) as that obtained in pyrex ampoules at this temperature (table on page 5 of Ref. 4).

Sample	Ampoule	Temperature	Average Rate, percent decomposed per hour		
			1.5 mm	2.0 mm	3.0 mm
Olin Mathieson Purified	Pyrex	171 C			0.0075
RPL Purified	Pyrex	171 C			0.0075
Olin Mathieson Purified	Pyrex	210 C	0.087	(0.065)*	(0.043)
Olin Mathieson Purified	Quartz	210 C	(0.080)	0.060	(0.040)
RPL Purified	Quartz	275 C	(0.070)	(0.052)	0.035

*Values in parenthesis are corrected for internal diameter of ampoule, assuming the rate is inversely proportional to the diameter.

The rate of decomposition of the RPL purified hydrazine was measured at 275 C (527 F) in 3 mm ID quartz ampoules in an attempt to reach conditions where the homogeneous liquid-phase decomposition would predominate. The average amount decomposed in seven 13-hour experiments was only 0.45 percent, with an average scatter of ±20 percent. It may be seen from the table above that this rate is approximately equivalent to that obtained with the Olin Mathieson Chemical Corporation purified material at 210 C.

The simplest explanation of these results, pending further investigation, is that: (1) quartz and pyrex surfaces have a similar activity toward hydrazine decomposition, (2) the Olin Mathieson Chemical Corporation purified hydrazine decomposes on glass with an activation energy of 19 kcal/mole, and (3) the RPL purified hydrazine decomposes with an activation energy of only 7 kcal/mole.

These results at 275 C establish the high inherent thermal stability of purified hydrazine and demonstrate that attempts to use hydrazine in high-temperature environments are warranted (for example, by eliminating deleterious impurities or by using more compatible materials of construction). The low activation energy obtained with the RPL purified hydrazine suggests that the homogeneous decomposition is very slow even at 527 F.

Propellant-Grade Hydrazine

It was reported previously that a reproducibility problem was encountered with some of the decomposition studies on metal surfaces at temperatures around 128 C (Fig. 2, Ref. 4). In investigating this problem, it was found that abnormally high blanks (no metal present) were obtained in some experiments at 128 C (up to 2.2 percent decomposed in 100 hours). This could account for some of the scatter observed with metals. No major reproducibility problems were found previously in blank runs at 171 or 95 C.

Prepassivations of the pyrex ampoules were investigated to determine if the abnormally high blanks could be eliminated in future experiments. The ampoule cleaning procedure was the same as before (clean in aqua regia, rinse in distilled water, dry), except that propellant-grade hydrazine was placed in the ampoules for 3 hours at room temperature before the final rinse. Eighteen blank runs have now been made at 128 C using this procedure, with "normal" rates being obtained in every case, i.e., less than 0.5-percent decomposition at heating times up to 120 hours. It appears that more than a simple passivation is involved--possibly some material is dissolved from the surface of the glass.

Effect of Ullage

The effect of varying the ullage-to-liquid ratio was investigated in eight passivated pyrex ampoules at 128 C with propellant-grade hydrazine. Within experimental error, the percent decomposed remained constant even though the ullage-to-liquid ratio was varied by a factor of 30. These results confirm that the decomposition occurs primarily in the liquid phase. This was established previously at 171 C.

Solvent Studies

Experiments were conducted to determine the kinetics of the liquid-phase decomposition of hydrazine when diluted in inert solvents. The goal was to determine the combined effect of dielectric constant and hydrazine concentration on the decomposition kinetics. The use of solvents of high and low dielectric constant should permit the two effects to be separated. If the decomposition rate is strongly dependent on the dielectric constant of the mixture, an ionic mechanism may be indicated.

Hydrazine was found to be completely miscible with both aniline and propylene carbonate (PC); however, the initial addition of small amounts of hydrazine to PC results in the evolution of a large amount of heat. Ampoules (3 mm ID pyrex) containing PC and aniline, respectively, were heated for 72 hours at 171 C. Only negligible amounts of noncondensable gas were measured in duplicate experiments with both solvents, indicating that either is sufficiently thermally stable for use as a diluent for hydrazine. The PC may not be suitable, however, because it interacts strongly with hydrazine (heat evolution during mixing) and its very slow rate of vaporization makes measurement of the noncondensables formed difficult.

Solvent studies were conducted with both propellant-grade hydrazine and the RPL purified hydrazine in the solvent aniline (dielectric constant of 6.89 at 20 C and 4.54 at 185 C). Solutions containing various concentrations of hydrazine in aniline were prepared (at least three at each concentration), and the ampoules (3 mm ID pyrex) heated at 171 C for 66 hours. The reproducibility was better with most of the solutions than with the neat hydrazines. The following average results were obtained:

Percent Hydrazine in Aniline	Hydrazine Concentration, moles/liter	Average Percent Decomposed	
		Propellant Grade	Purified
20	6.3	1.86	0.44
40	12.5	1.81	0.38
60	18.8	1.15	0.29
80	25.1	1.15	0.28
100	31.3	1.27	0.30

The propellant-grade hydrazine decomposes about four times faster than the purified hydrazine at all concentrations.

If the decomposition rate were only a function of hydrazine concentration,

$$R = k(\text{Hz Conc})^n$$

where n is the apparent reaction order with respect to hydrazine, a plot of log $\left[-d(\text{Hz Conc})/dt\right]$ vs log (Hz Conc) should be linear with a slope equal to n. The aniline results are plotted in this form in Fig. 1 (a constant volume of solution is present in each ampoule so the rate of production of gaseous products is proportional to the rate of decrease of hydrazine concentration). A nearly linear plot is obtained with each hydrazine except that the first 20-percent aniline added had a slightly greater effect. Surprisingly, the same apparent reaction order of about 2/3 was obtained for both the propellant-grade and purified hydrazines.

Because the dielectric constant of the solution changes with hydrazine concentration , it can be shown that, if the rate is independent of the dielectric constant of the mixture (which decreases by about a factor of 3 in going from pure hydrazine to the 20-percent solution in aniline), the mechanism must be in agreement with the rate expression:

$$R = k(\text{Hz Conc})^{2/3}$$

If, conversely, the rate is directly proportional to the dielectric constant, it can be shown that the rate must be independent of the hydrazine concentration (i.e., zero order):

$$R = k(\epsilon)^1(\text{Hz Conc})^0 = k\epsilon$$

Any expression between these limiting cases would fit the observed results. In other words, the results indicate that the rate cannot be a simultaneously strong function of both the dielectric constant and the concentration of hydrazine.

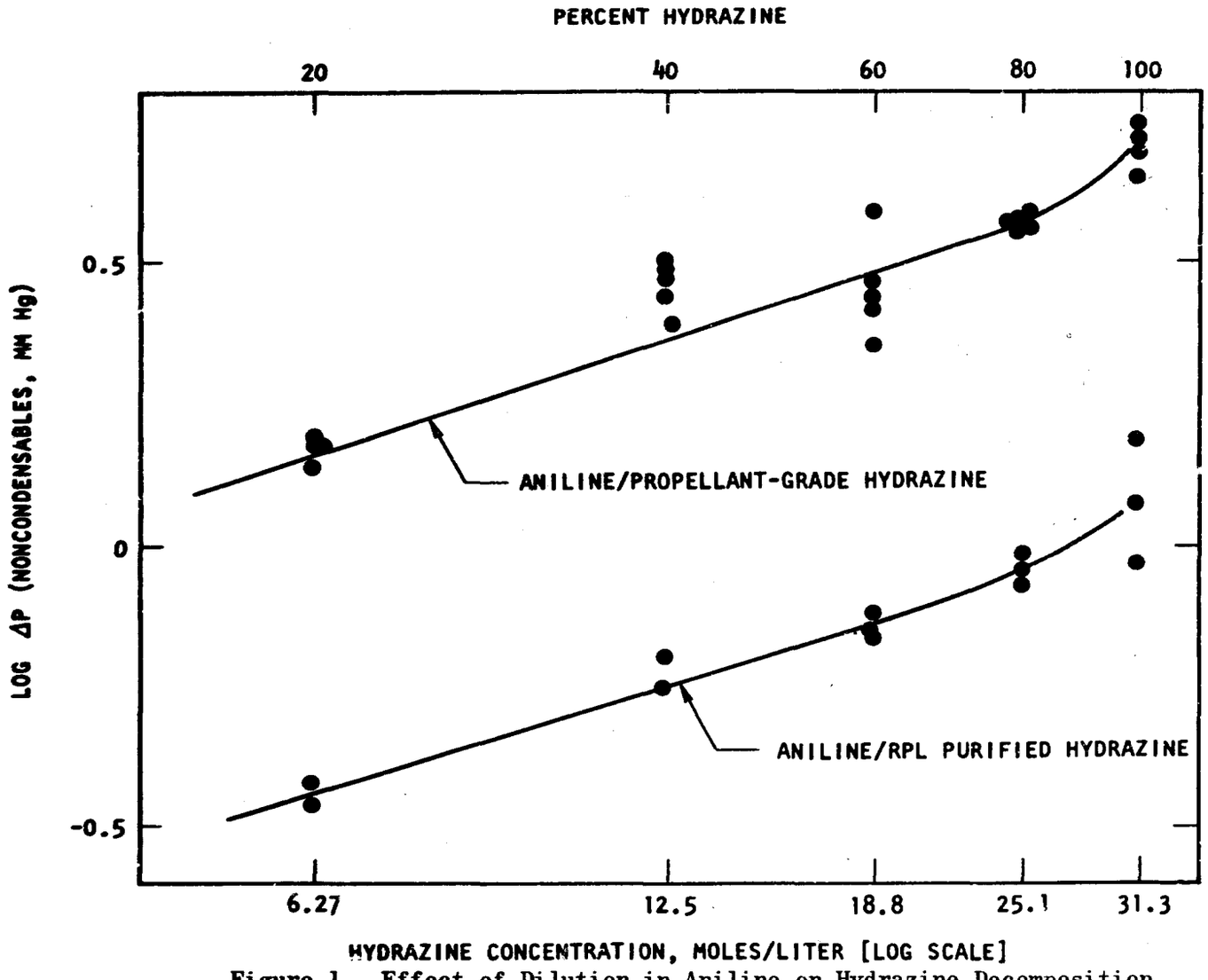

Figure 1. Effect of Dilution in Aniline on Hydrazine Decomposition Rate (171 C, 66 Hours, Pyrex Ampoules)

It was quite unexpected that both the purified and propellant-grade hydrazines should have nearly identical apparent reaction orders in an aniline solution. Because the decomposition of purified hydrazine in glass ampoules has been demonstrated previously to be a surface reaction, a zero-order ionic reaction with a first-order dependence on the dielectric constant is quite possible. It is unlikely, however, that the rate of the impurity-catalyzed decomposition of propellant-grade hydrazine will have a low dependence on the hydrazine concentration. Therefore, the results indicate that the propellant-grade hydrazine decomposes by a mechanism which is nearly independent of the dielectric constant of the solution.

EXPERIMENTAL TECHNIQUES

The gas-measuring system and the experimental techniques were described in Ref. 2. The reactors are sections of heavy-walled capillary tubing sealed at each end. The reactors are usually 2.5 mm ID, approximately 13 centimeters in length, and contain 0.3 milliliter of hydrazine. The normal ullage volume is on the order of 40 percent of the reactor volume in most experiments.

TASK II: HETEROGENEOUS DECOMPOSITION ON METAL SURFACES

The study of the decomposition of liquid hydrazine on metal surfaces was continued with emphasis on the effect of the method of surface treatment. The experiments were conducted in sealed pyrex ampoules with a metal specimen of 1 cm^2 geometric surface area present in the liquid phase.

RESULTS AND DISCUSSION

A series of 48-hour experiments was run at 110 C with propellant-grade hydrazine and 347 stainless steel to investigate the effect of the method of cleaning the metal surface. The pyrex ampoules were not prepassivated. In the first six experiments, the metal was cleaned with boiling nitric acid; the average decomposition was 2.1 ±1.1 percent. In the other six experiments, the surface was cleaned with trichloroethylene; the average decomposition was only 0.67 ±0.21 percent. The scatter in the data was excessive in each series.

It was reported in Ref. 4 that acid-cleaned 347 stainless steel in propellant-grade hydrazine gave decomposition rates at 128 C which were not linear with time and were quite nonreproducible at a given heating time of 40 hours. These results are presented as the first series of experiments in Table 1 for comparison.

The 17- and 64-hour experiments at 128 C listed in Table 1 were conducted to determine the effect of various treatments of the 347 stainless-steel surface. In the 17-hour experiments, the metal was boiled in trichlor and then in acetone; very high decomposition rates were obtained. It was then discovered that many of the blank runs (no metal) were giving high rates at 128 C and that this could be prevented by passivating the glass surface with hydrazine at room temperature. This technique was tried on the 347 stainless-steel surface in the first series of 64-hour experiments (Table 1). Much lower rates were obtained than with the previous cleaning techniques, but additional experiments will be required at 128 C with trichlor alone to establish definitely the effect of prepassivation with hydrazine.

TABLE 1

EFFECT OF SURFACE TREATMENT ON DECOMPOSITION RATE OF HYDRAZINE ON 347 STAINLESS STEEL AT 128 C

Propellant	Hours	Percent Decomposed	Percent Decomposed (adjusted to 40 hours)*	Average	Surface Treatment	
					Metal	Ampoule
Propellant Grade (Lot 104)	4.5	0.073	0.65	0.65	HNO_3	Aqua Regia
	11.5	0.18	0.63	0.63		
	23.5	2.2	3.7	3.7		
	31.5	0.86	1.09	1.09		
	40	4.5	4.5	2.2		
	40	1.5	1.5			
	40	0.86	0.86			
	40	1.8	1.8			
	40	2.3	2.3			
	48	1.28	1.07	1.07		
	72	3.9	2.2	2.2		
	144	2.1	0.58	0.58		
Propellant Grade (Lot 104)	17	4.6	10.8	16.6	Boil Trichlor + Boil Acetone	Aqua Regia
	17	7.2	17.0			
	17	>8.8	20.7			
	17	6.2	14.6			
	17	8.5	20.1			
Propellant Grade (Lot 104)	64	0.90(A)**	0.56	0.81	Boil Trichlor + Hz Passivated	Aqua Regia + Hz Passivated
	64	1.09(B)	0.68			
	64	1.10(C)	0.69			
	64	1.22(D)	0.76			
	64	1.72(E)	1.07			
	64	1.72(F)	1.07			
Propellant Grade (Lot 104)***	64	0.27(A)	0.17	0.20	Boil Trichlor + Hz Passivated***	Aqua Regia + Hz Passivated
	64	0.31(C)	0.19			
	64	0.34(D)	0.21			
	64	0.34(E)	0.19			
	64	0.40(F)	0.25			
Purified (Olin Mathieson)	40	0.30	0.30	0.70	HNO_3	Aqua Regia
	40	1.23	1.23			
	40	0.58	0.58			

*For comparison purposes, assume rate is linear with time
**Letter designates individual metal specimen
***Rerun of above metal specimens after recleaning in boiling trichlor and repassivating with room temperature hydrazine

The lack of reproducibility from ampoule to ampoule could result from an actual nonuniformity of the surfaces of the metal specimens. To test this, the metal specimens used in the 64-hour experiments were recleaned and passivated, and rerun with propellant-grade hydrazine (Table 1). A direct correlation could not be established between the relative activities of given specimens in the first and second runs. It was found, however, that the average decomposition rate in the second series of 64-hour experiments was only one-fourth that of the first 64-hour runs. It appears that contacting the metal with hydrazine and/or its decomposition products at 262 F further passivates the surface (this must be established by further experiments, however, because this rate is lower than that obtained in some blank runs without metal under these conditions). The average rate obtained in the second series of 64-hour experiments (0.2 percent per 40 hours) is 1 order of magnitude lower than the rate with acid-cleaned specimens, and 2 orders of magnitude lower than with trichlor/acetone-cleaned 347 stainless-steel specimens.

The last three experiments (Table 1) were conducted with purified hydrazine and 347 stainless steel. A very large scatter in the results was obtained. Comparison of these experiments with the 40-hour experiments using propellant-grade hydrazine (Table 1) indicates that the purified hydrazine gives a lower rate when compared under identical conditions. It may be seen from Fig. 2 that very low decomposition rates of only about 0.1 percent per 40 hours are obtained with purified hydrazine and 321 stainless steel passivated with room-temperature hydrazine.

A final series of experiments was run at 128 C to compare the relative catalytic activities of several metal surfaces which had been passivated in hydrazine for three days at room temperature (after cleaning in boiling trichlor). The following results were obtained with propellant-grade hydrazine and a heating time of 75.5 hours:

Specimen	Percent Decomposed	Specimen	Percent Decomposed	Specimen	Percent Decomposed
Chromel A	1.09	321 Stainless Steel	0.47	Fe	Broke
	2.64		0.45		
	2.13		0.57		
	2.12		0.51	Ni	Broke
Cu	1.10	316 Stainless Steel	3.40		
	0.89		2.67	None	0.26
	0.90		2.92		0.36
	0.97		4.12		0.32
Al	0.97	304 Stainless Steel	0.92		
	0.57		0.60		
	0.58		0.87		
	0.74		1.12		
	0.84				
	0.68				

It was unexpected that aluminum would be more active than 321 stainless steel because aluminum had shown no effect over pyrex at 171 C (Ref. 4, Table 1). It may be that aluminum requires a nitric acid passivation.

EXPERIMENTAL TECHNIQUES

The same procedure is used for this task as for the experiments under Task I, except that a metal specimen is present in the liquid phase. In a typical experiment, the ampoules are 2.5 mm ID and 10 cm in length, the internal volume is 0.5 ml, and 0.3 ml of liquid hydrazine is present. The metal specimens are usually in the form of 1/16-inch OD tubing with a surface area of about 1 cm^2. The reported rates were corrected to 1 cm^2 of surface.

The ampoules are cleaned in aqua regia, rinsed in distilled water, and dried. Passivation of the ampoules in room-temperature hydrazine has been employed in some experiments. Several methods have been used to clean and passivate the metal surfaces. The liquid sample is repetitively outgassed on a vacuum line before the ampoule is sealed with a torch.

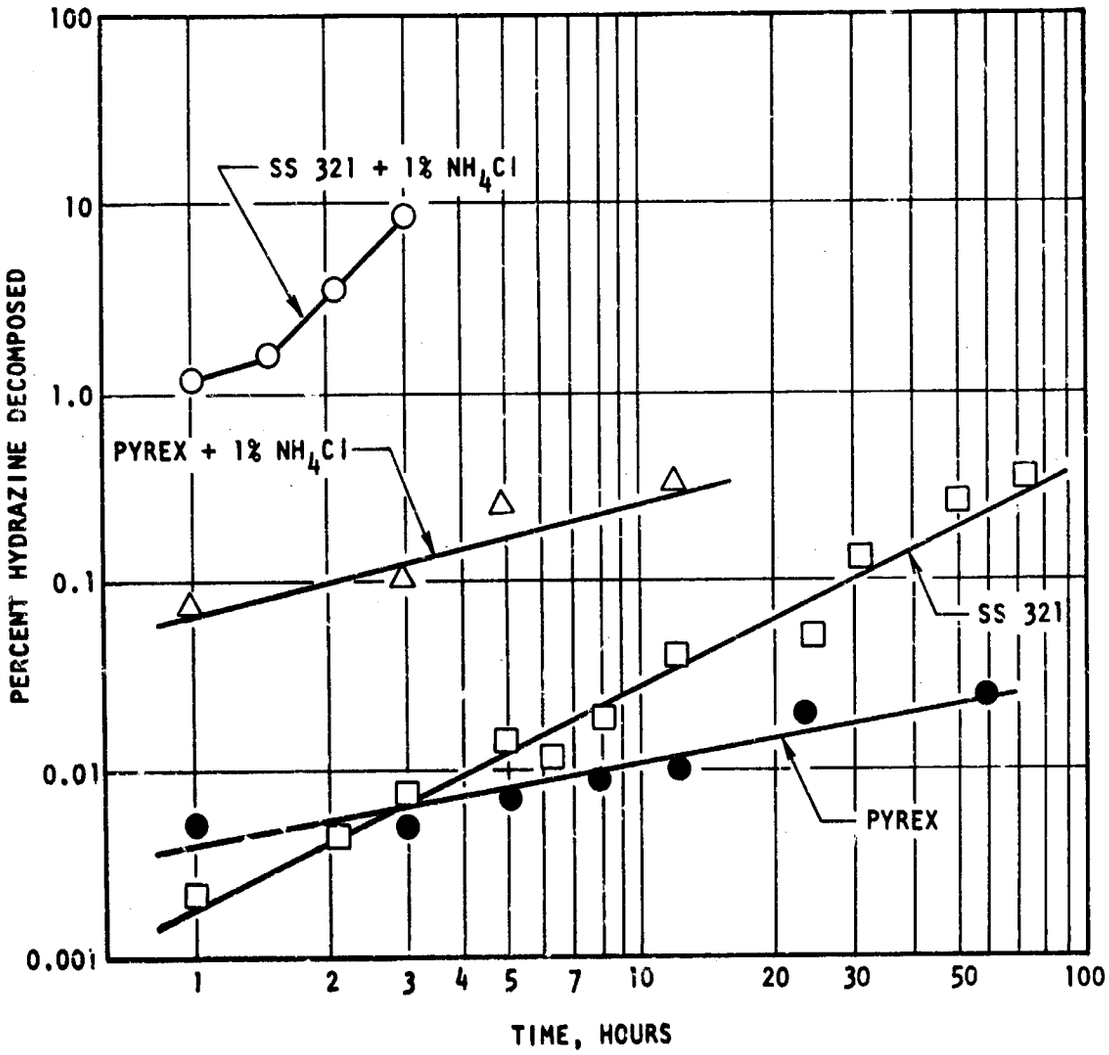

Figure 2. Effect of Added NH_4Cl on Decomposition Rate of RPL Purified Hydrazine on Pyrex and 321 Stainless Steel at 128 C

The air bath has been replaced with an oil bath to reduce temperature gradients in the ampoule. This reduces the tendency of the liquid hydrazine column to separate, leaving part of the metal surface out of contact with the liquid. After an ampoule has been removed from the heating bath, it is broken in a vacuum system and the products that are noncondensable at -196 C are measured and analyzed.

TASK III: ROLE OF IMPURITIES

It may be seen from the differences in the thermal stabilities of the propellant-grade and purified hydrazines that one or more of the impurities present in propellant-grade hydrazine causes its lower thermal stability. The impurities in hydrazine previously identified in this program are H_2O, NH_3, aniline, toluene, and iron. In addition to these impurities, an unidentified impurity is present in the propellant-grade hydrazines at the 100- to 400-ppm level (Ref. 1), and a different, unidentified impurity (carbon-containing) is present in the Olin Mathieson Chemical Corporation purified hydrazine at about 100 ppm (Ref. 2).

Various known hydrazine impurities were previously added to the Olin Mathieson Chemical Corporation purified hydrazine and the effect on the decomposition rate at 171 C measured (Ref. 3). Aniline had no effect at 0.5 and 1.2 percent. In fact, when up to 40-percent aniline was added to the RPL purified hydrazine for another purpose in the solvent studies (Task I), the percentage of hydrazine decomposed in 66 hours remained essentially unchanged. Toluene at 400 ppm may have caused a small increase in rate, but the rates obtained were within the experimental scatter. The impurity NaCl, reported as a trace impurity in some hydrazines, also had no effect on the decomposition rate when added at 20 ppm.

The addition of distilled water to the Olin Mathieson Chemical Corporation purified hydrazine, however, did increase the decomposition rate appreciably (by a factor of 3.4 at 90 hours), but the effect was nearly independent of the amount of water added (Ref. 3). The addition of 0.5- to 2.1-percent water gave extents of decomposition after 20 and 90 hours about half-way between those obtained with the propellant-grade and purified hydrazines.

RESULTS AND DISCUSSION

Analysis of RPL Purified Hydrazine

It was reported under Task I that hydrazines purified by Olin Mathieson Chemical Corporation and AFRPL by different procedures decomposed at about the same rate. Previous analyses of the Olin Mathieson Chemical Corporation material (Ref. 2) indicated that it contained 99.7-percent N_2H_4, ~0.2-percent H_2O, ~0.1-percent NH_3, 49 ppm aniline, and no toluene. The following analysis was obtained on the RPL purified material during this report period:

Sample	Aniline, weight percent	NH_3, weight percent	H_2O, weight percent	Toluene, ppm	N_2H_4, percent	
					Difference	Assay
RPL Purified Hydrazine, Sample 1	0.26	< 0.01	0.38	2.7	99.36	99.3
RPL Purified Hydrazine, Sample 2	0.15	< 0.01	0.24	<1.0	99.61	99.6

The main difference between the two purified hydrazines (Olin Mathieson Chemical Corporation and RPL) is their aniline content. It was shown previously that aniline does not catalyze the decomposition reaction.

Olin "Mother Liquor"

A sample was received of the mother liquor from the Olin Mathieson Chemical Corporation purification process. This material would be expected to contain more impurities than even propellant-grade hydrazine. It was run in six pyrex ampoules for 20 hours at 171 C. Three of the ampoules broke and the remaining three gave decompositions of 1.3, 1.6, and 1.3 percent, respectively. This is nearly twice the rate at which propellant-grade hydrazine decomposes under these conditions.

A recent analysis of this material gave the following results: 94.5-percent N_2H_4, 4.7-percent H_2O, 0.03-percent NH_3, 0.74-percent aniline, and 26-ppm toluene.

Added Carbazic Acid

The effect of the addition of 1 weight percent carbazic acid, $NH_2NHCOOH$, on the decomposition rate of the RPL purified hydrazine was investigated. The pyrex ampoules (3 mm ID) were prepassivated with propellant-grade hydrazine at ambient temperature. The reaction time was 66 hours at 171 C with the following results:

Sample	Percent Decomposed
Neat Purified Hydrazine	0.36, 0.44, 0.33, and 0.34
Purified Hydrazine + 1-percent Carbazic Acid	2.00 and 2.04 (two ampoules broke)

It may be seen by comparison with Fig. 1 of Ref. 3 that the purified hydrazine containing carbazic acid decomposes at about the same rate as does propellant-grade hydrazine.

The measured stoichiometry of the carbazic acid catalyzed decomposition was the same as that obtained with the neat purified hydrazine in prepassivated ampoules:

$$N_2H_4 \longrightarrow 1.26\ NH_3 + 0.37\ N_2 + 0.11\ H_2$$

Carbon dioxide is known to react rapidly with hydrazine (neat or aqueous solution) to form carbazic acid which, in the presence of excess hydrazine, forms the salt, $N_2H_3COON_2H_5$. Therefore, the addition of 1 weight percent carbazic acid to hydrazine results in the same final solution as would be obtained by allowing 0.58 percent CO_2 to react with hydrazine. The carbazic acid used in this study was prepared for another purpose in a current Rocketdyne IR&D study by reacting an aqueous solution of hydrazine with an excess of carbon dioxide.

It is expected that the hydrazine salt of carbazic acid will ionize in hydrazine as $N_2H_5^+$ and $N_2H_3\ COO^-$. If the $N_2H_5^+$ ion is the reactive or catalytic species in the carbazic acid catalyzed decomposition of hydrazine, this would be in agreement with the previous observation that, of the other additives tested, only water increased the decomposition rate. The hydrazine hydrate also would be expected to ionize partially to $N_2H_5^+$ in hydrazine ($N_2H_5OH \longrightarrow N_2H_5^+ + OH^-$). This possible ionic mechanism was tested further by adding other acids to hydrazine (see below).

An indirect gas chromatographic technique for the detection of carbazic acid (N_2H_3COOH) in liquid hydrazine has been demonstrated as feasible. The method is based on the liberation of CO_2 from the reaction of carbazic acid with strong acids. A heated, "on-column" injection port was installed on the Perkin-Elmer 154-C gas chromatograph to permit direct syringe introduction of hydrazine samples into sulfuric acid-impregnated silica-gel. The instrument is equipped with dual, parallel molecular sieve/silica-gel columns and dual, series thermistor/d-c discharge detectors for general fixed gases analyses.

Standards were prepared using carbazic acid in hydrazine in concentrations of 0.01, 0.1, and 1.0 weight percent. Injection of the standards and the neat hydrazine revealed that order-of-magnitude differentiation was readily accomplished, but that the acidified material in the injection port was soon neutralized sufficiently to yield nonreproducible CO_2 peaks. Reaction stoichiometry was verified within an order of magnitude by comparison with injections of a 10-ppm CO_2 standard in helium. Detection is accomplished at the submicromole levels.

Examination of hydrazine samples currently undergoing general analysis showed that the propellant-grade fuel released approximately 10 times as much CO_2 as the RPL purified fuels. Nonreproducibility precluded quantification. Comparison with the standards indicated the level to be approximately 0.01-percent carbazic acid in the purified fuels. Reproducibility improvement will require design and fabrication of an injection port which would place more acid in the injection region; this modification is in progress.

These results suggest that carbazic acid may be one of the unidentified impurities contributing to the reduced thermal stability of propellant-grade hydrazine. This possibility is being investigated further.

Added HCl

It is of interest to determine if acids other than carbazic acid are effective in decreasing the stability of hydrazine. Solutions containing 1 weight percent HCl were prepared by adding concentrated HCl (Allied 37.5 percent) to the Olin Mathieson Chemical Corporation purified hydrazine. Because the addition of 1-percent HCl by this method entailed the incidental addition of 1.6-percent H_2O, samples also were prepared containing this concentration of H_2O. After 2.8 hours at 171 C in pyrex ampoules, the acidified sample had undergone 4.6-percent decomposition, while the unacified sample had decomposed only 0.08 percent. A "blank" sample which contained no added HCl or H_2O gave only 0.02-percent decomposition. Thus, the addition of 1 weight percent HCl increases the percentage decomposition by a factor of 50 over that for a sample containing an equivalent amount of water, and a factor of 200 over that for the neat hydrazine. Apparently, HCl is more effective than carbazic acid in reducing the stability of hydrazine. However, it should be noted that its molar concentration was approximately twice as high, and a different purified hydrazine was used.

Added NH_4Cl

A series of experiments was conducted to determine the effect of 1 weight percent NH_4Cl on the rate of decomposition of RPL purified hydrazine. The addition of NH_4Cl should be equivalent to the addition of HCl because the following reaction occurs: $NH_4Cl + N_2H_4 \longrightarrow N_2H_5Cl + NH_3$. The NH_3 is pumped off during the degassing procedure. The percentage decomposition was followed as a function of time at 128 C.

The results shown in Fig. 2 indicate that 1-percent NH_4Cl increases the rate in the absence of metal by about a factor of 20. The same effect was obtained with 1-percent carbazic acid.

The effect of added NH_4Cl in the presence of a metal surface was investigated next. It may be seen from Fig. 2 that the effect is much greater on a 321 stainless-steel surface than in the absence of a metal surface. The decomposition after 3 hours on 321 stainless steel is increased by more than a factor of 1000 by the addition of 1-percent NH_4Cl. The rate in the presence of the additive is increasing nearly exponentially with time, indicating that all of the hydrazine would have decomposed in a few more hours. Tests are in progress to determine if the catalytic effect of carbazic acid also is markedly enhanced by the presence of a metal surface. Conductivity studies will be carried out to determine the relative degrees of ionization of N_2H_5Cl and $N_2H_5OOCN_2H_3$ in hydrazine. This will give an indication of the possible roles of the $N_2H_5^+$ and Cl^- ions in the decomposition mechanisms.

Added NH_3

The effect of adding NH_3 to propellant-grade hydrazine was investigated at higher NH_3 concentrations to determine if the NH_3 formed during decomposition inhibited the reaction. Quartz reactors of 1 mm ID were used to prevent breakage. The heating time was 22 hours in all experiments at a temperature of 171 C.

These are the only experiments which have been conducted in quartz with propellant-grade hydrazine. The blank runs (no added NH_3) gave percent decompositions of 1.6, 1.9, 1.5, and 1.1. These are higher than the value of 0.8 percent usually obtained in 3 mm ID pyrex ampoules. Because the decomposition of propellant-grade hydrazine is partly heterogeneous at 171 C (page 7, Ref. 3), much of this difference can be accounted for by the higher surface-to-volume ratio of the 1 mm ID capillary. However, it appears also that liquid propellant-grade hydrazine decomposes somewhat faster on a quartz surface than on a pyrex surface.

Three runs were made under the same conditions as above with 7.8-percent NH_3 added to propellant-grade hydrazine. One ampoule broke and the other two samples of hydrazine underwent decompositions of 1.3 and 1.6 percent, respectively. It appears, therefore, that NH_3 had no effect on the decomposition rate, and its buildup as a product does not cause the observed decrease in decomposition rate with time (Fig. 1, Ref. 3).

Analysis of Propellant-Grade Hydrazine

A new sample of the Lot 104 propellant-grade hydrazine (Lot 104-3) in use at Rocketdyne was recently analyzed. It was found to contain 98.4-percent N_2H_4, 0.70-percent H_2O, 0.18-percent NH_3, 0.66-percent analine and 200 ppm toluene.

Reaction Stoichiometry

The decomposition of hydrazine can, in theory, result in the formation of varying amounts of NH_3 from 4/3 moles per mole of N_2H_4 decomposed to none. The generalized stoiochiometry equation is usually written as:

$$N_2H_4 \longrightarrow \frac{4}{3}(1-f)\ NH_3 + \frac{1}{3}(1 + 2f)\ N_2 + 2f\ H_2 \qquad (1)$$

where f is referred to as the "fraction of ammonia decomposed." Equation 1 differs slightly from the form presented in Ref. 1, but the form used here is more common.

In the present program, the measured quantities are the ratio of H_2 to N_2 (R) and the total moles of noncondensable products (N_2 +H_2). The value of f can be calculated as follows:

$$f = R/(6-2R) \qquad (2)$$

The amount of hydrazine decomposed is calculated from the measured amount of noncondensable gas as follows:

$$\text{moles } N_2H_4 = [3/(1 + 8f)]\ (\text{moles } N_2 + \text{moles } H_2) \qquad (3)$$

The decomposition of hydrazine vapor at very high temperatures, such as those encountered in a shock tube or decomposition flame, normally follows a stoichiometry corresponding to a value of f of 0.25 (or greater). Also, it is usually assumed that the decomposition of hydrazine vapor on the Shell 405 catalyst follows a stoichiometry in which f equals 0.25. However, the highest values of f obtained in the current program for the decomposition of liquid hydrazine at temperatures up to 527 F is only 0.11. The lower amounts of hydrogen produced in the liquid-phase decomposition could result from an entirely different decomposition mechanism (e.g., ionic) or from a free radical mechanism similar to that which obtains in the vapor phase except that a high activation energy process does not occur at the lower temperatures. For example, in the high-temperature vapor-phase decomposition, hydrogen and nitrogen have been postulated to form in equal amounts from the decomposition of the N_2H_3 radical:

$$N_2H_3 \longrightarrow N_2 + H_2 + H$$

At lower temperatures, the major fate of the N_2H_3 radical may be:

$$N_2H_3 + NH_2 \longrightarrow NH_3 + N_2H_2$$

$$N_2H_2 \longrightarrow N_2 + 2H$$

$$H + NH_2 + M \longrightarrow NH_3 + M$$

in which case nitrogen and ammonia would form without the concurrent production of molecular hydrogen.

Because the decomposition of hydrazine can have a variable stoichiometry, it is likely the stoichiometry obtained under a specific condition will be helpful in elucidating the respective decomposition mechanism. The stiochiometries observed (on this program) for the liquid-phase decomposition of hydrazine under various conditions always give mainly NH_3 and N_2, with the presence of minor amounts of H_2. Although some exceptions exist, the following are typical stoichiometries:

Conditions	Percent Hydrogen in Noncondensables*	Percent Ammonia Decomposed (100 x f)
Propellant Grade/No Metal	2 to 15	0.3 to 3.1
Olin Mathieson Purified/No Metal	14 to 30	2.9 to 8.3
RPL Purified/No Metal	13 to 25	2.6 to 6.2
Propellant Grade in Aniline	9 to 14	1.7 to 2.9
RPL Purified in Aniline	5 to 16	0.9 to 3.4
Propellant Grade/Metal		
SS 304, 316, 321, 347 Fe, Ni, Be, Chromel A, Cu	0.6 to 8	0.1 to 1.5
Al	1.0 to 34	0.17 to 10.5

*Remainder is nitrogen

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The kinetics of the decomposition of liquid hydrazine was investigated in sealed ampoules. The effects of temperature, hydrazine purity, and type of metal surface present were studied.

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