Interactions of Hydrazine and Blowby Gases

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ABSTRACT

The interactions between hydrazine and blowby gases from pyrovalves was explored in this research project. Investigating the decomposition chemistry of hydrazine through detailed chemical kinetic modeling is a project started last summer while participating in the Summer Faculty Fellowship program. During the 1999-2000 academic year, the chemical kinetic mechansim for hydrazine decomposition developed while a SFF at NASA's White Sands Test Facility was further revised and validated against the limited experimental data in the literature. This mechanism was then used in assessing the effects of blowby gas species on hydrazine decomposition.

The combustion products introduced into the fuel line by pyrovalve actuation consist primarily of hydrogen gas. Hydrogen is also a product of the decomposition of hydrazine. Additional gaseous chemical species are introduced into the fuel, as well as metals and metal salts that deposit onto the walls of the fuel line. The deposition process is undoubtedly very rapid, and exothermic. Therefore, the major focus of this summer's work was examining the effects of hydrogen presence on hydrazine decomposition, with some representative calculations including the remaining gaseous species found to exist in blowby gases.

Since hydrogen is a product of hydrazine decomposition, all reactions necessary to evaluate its effect on hydrazine decomposition chemistry were in the original mechanism developed. However, the mechanism needed to be considerably expanded to include the reactions of the other gaseous blowby species with hydrazine, all the intermediate species formed in its decomposition, and each other. The expanded mechanism consists of 70 species interacting via a network of 452 reactions.

Calculations with molecular hydrogen introduced into hydrazine gas in an inert bath gas indicate that H_2 presence as an initial reactant in substantial amounts can dramatically impact the decomposition process for hydrazine. The other gaseous blowby species (CO, CO_2, H_2O, CH_4, O_2, and N_2) were found to have little effect compared to the inclusion of hydrogen itself as an initial reagent. This result is undoubtedly due, in part, to the fact that the blowby gas used in these calculations consisted of 94.6% H_2. A more rigorous examination of the behavior of the full detailed mechanism under a variety of conditions was not performed.

INTRODUCTION

Hydrazine decomposition has been the subject of scientific study for a considerable time.[1-10] The final products of hydrazine decomposition change with the temperature at which the decomposition is initiated. N_2H_4 decomposition can be described by the following two reactions:

$$2\,N_2H_4 \rightarrow 2\,NH_3 + N_2 + H_2 \qquad \Delta H_r = -141.3\ \text{kJ/mol}\ N_2H_4 \qquad \text{(R1)}$$

$$N_2H_4 \rightarrow N_2 + 2\,H_2 \qquad \Delta H_r = -95.4\ \text{kJ/mol}\ N_2H_4 \qquad \text{(R2)}$$

Experimentalists have noted that at lower initial temperatures, the decomposition of hydrazine is dominated by R1, while at higher temperatures, the product mixture observed is more accurately represented by R2.

The study of hydrazine decomposition is of basic scientific interest, however, the main reasons for this study are found in the results of research conducted at NASA's White Sands Test Facility (WSTF). The Mars Observer failure review board indicated that propulsion and pyrotechnic systems may have contributed to the loss of the spacecraft.[11] Experiments performed at WSTF revealed that pyrovalve actuation could result in uncontrolled fuel decomposition which fragmented a simulated fuel line.[12-14] These results suggested that a more thorough understanding of the decomposition chemistry of N_2H_4, and the potential effects of blowby gases on the process, is needed.

Actuating a pyrovalve is known to introduce combustion products from the valve into the fuel line. Although the valves are designed to minimize the contamination of the fuel system, some gases escape the combustion chamber in the valve. These hot gases entering the fuel system will result in both a localized temperature increase in the fuel as well as an alteration of the chemical composition of the fuel or fuel vapors immediately adjacent to the valve. WSTF has designed and produced a pyrovalve simulator connected to instrumentation capable of measuring pressure increases in an evacuated line upon valve cycling, and more importantly, chemical species escaping the confines of the combustion chamber.[15]

The chemical species measured in the blowby gases provided a starting point for a chemical kinetic analysis of possible chemically, rather than thermally, initiated local decomposition near the pyrovalve that could ultimately result in a thermal runaway of the fuel. It is highly likely that both thermal and chemical effects from the interaction of the blowby gases with the fuel resulted in the observed destruction of simulated fuel lines. The importance of understanding the chemistry of N_2H_4 decomposition must not be forgotten while focusing on the interaction of blowby gases and hydrazine; interactions between the blowby gases and hydrazine will be a very localized phenomenon near the pyrovalve. Propagation of fuel decomposition will result from the chemistry of the fuel itself, combined with various physical factors within the fuel system.

EXPERIMENTAL

The decomposition mechanism developed last summer was further updated in February of 2000 by the addition of a chemical species and its associated reactions overlooked in the earlier mechanism. A revision of some of the rate

expressions in the first version of the mechanism was also completed. This fully updated mechanism for the N/H system was used in modeling the interactions of hydrazine and hydrogen gas. The majority of the rate expressions were obtained from Ref. 16 or primary references therein. This mechanism comprises 12 species interacting in a network of 51 elementary reactions (not counting duplicates); it was validated during the 1999-2000 academic year. Although a fair number of experimental studies have been published in the open literature, the amount of reliable thermal decomposition data available for mechanism validation is rather limited. Nonetheless, the mechanism proved to be quite accurate at modeling the decomposition process of hydrazine in a diluent gas in the temperature regime typical of shock-tube studies.[17]

The mechanism used for the modeling work completed this summer is presented in Table 1. Due to space considerations, the larger, more inclusive mechanism for all blowby species will not be presented in this report.

Table 1. N/H Mechanism for Hydrazine Decomposition

Reactions Considered	k = A T**b exp(-E/RT))		
	A	b	E
1. NH2+NH2=N2H4	3.200E+49	-11.18	13988.0
2. N2H3=HNNH+H	1.800E+45	-9.39	70141.0
3. HNNH=NNH+H	3.100E+41	-8.42	76102.0
Declared duplicate reaction...			
4. HNNH=NNH+H	1.300E+44	-9.22	77096.0
Declared duplicate reaction...			
5. HNNH=H2NN	1.300E+45	-10.13	77096.0
6. H2NN=NNH+H	5.100E+33	-6.52	54245.0
Declared duplicate reaction...			
7. H2NN=NNH+H	5.000E+36	-7.43	57226.0
Declared duplicate reaction...			
8. NNH=N2+H	3.000E+08	0.00	0.0
Declared duplicate reaction...			
9. NNH+M=N2+H+M	1.000E+13	0.50	3080.0
Declared duplicate reaction...			
10. NH3+M=NH2+H+M	2.200E+16	0.00	93470.0
N2 Enhanced by 1.500E+00			
11. NH2+M=NH+H+M	1.200E+15	0.00	76004.0
N2 Enhanced by 1.500E+00			
12. NH+M=N+H+M	2.650E+14	0.00	75510.0
N2 Enhanced by 1.500E+00			
13. N2H4+H=N2H3+H2	9.600E+08	1.50	4838.0
14. N2H4+H=NH2+NH3	4.460E+09	0.00	3100.0
15. N2H4=H2NN+H2	2.500E+39	-8.19	69744.0
16. NH2+NH2=N2H3+H	1.200E+12	-0.03	10084.0
17. N2H3+H=NH+NH3	1.000E+11	0.00	0.0

18. HNNH+H=NNH+H2	4.800E+08	1.50	1579.7
19. NNH+H=N2+H2	2.400E+08	1.50	-894.0
20. NH3+H=NH2+H2	5.420E+05	2.40	9917.0
21. NH2+H=NH+H2	4.800E+08	1.50	7938.0
22. N+H2=NH+H	1.600E+14	0.00	25140.0
23. N2H4+NH=NH2+N2H3	1.000E+12	0.50	1987.0
24. HNNH+NH=NNH+NH2	2.400E+06	2.00	-1192.0
25. H2NN+NH2=NH3+NNH	1.800E+06	1.94	-1153.0
26. NNH+NH=N2+NH2	5.000E+13	0.00	0.0
27. NH+NH=NH2+N	1.990E+11	0.50	1987.0
28. NH+NH=NNH+H	7.940E+12	0.50	994.0
29. N2H4+NH2=N2H3+NH3	3.700E+06	1.94	1629.0
30. N2H3+NH2=HNNH+NH3	9.200E+05	1.94	-1152.5
31. N2H3+NH2=H2NN+NH3	3.000E+13	0.00	0.0
32. HNNH+NH2=NNH+NH3	1.800E+06	1.94	-1152.5
33. HNNH+NH2=NH+N2H3	1.000E+11	0.50	33779.0
34. NNH+NH2=N2+NH3	9.200E+05	1.94	1152.0
35. NH3+NH2=N2H3+H2	7.940E+11	0.50	2146.0
36. NH2+NH2=NH+NH3	9.200E+05	1.94	2444.0
37. NH2+NH=HNNH+H	1.500E+15	-0.50	0.0
38. NH2+N=N2+H+H	7.200E+13	0.00	0.0
39. N2H4+HNNH=N2H3+N2	2.510E+10	0.50	9935.0
40. HNNH+N2H3=N2H4+NNH	1.000E+13	0.00	9935.0
41. HNNH+HNNH=NNH+N2H3	1.000E+13	0.00	9935.0
42. NNH+NNH=HNNH+N2	1.000E+13	0.00	9935.0
43. NH+N=N2+H	1.500E+13	0.00	0.0
44. NNH+N=NH+N2	3.160E+13	0.00	1987.0
45. NH+NH=N2+H+H	5.100E+13	0.00	0.0
46. N2+M=N+N+M	3.710E+21	-1.60	225000.0
47. H+H+M=H2+M	1.000E+18	-1.00	0.0
48. 2H+H2=2H2	9.200E+16	-0.60	0.0
49. N2H3+N=NH+HNNH	1.000E+13	0.00	2000.0
50. N2H4+N=N2H3+NH	1.000E+13	0.00	4000.0
51. N2H3+N=NH+H2NN	1.000E+13	0.00	2000.0
52. N2H3+H=H2NN+H2	2.400E+08	1.50	0.0
53. N2H3+H=HNNH+H2	2.400E+08	1.50	0.0
54. H2NN+H=H2+NNH	4.800E+08	1.50	-894.0

Computations were performed using the same computer software and hardware that was utilized last summer.[18] An additional computer program for producing pathway diagrams was also used.[19] The reader is directed to contact the authors of the pathways analysis code directly for obtaining the software.

Discussions with personnel at WSTF resulted in enough information to begin computations to predict the results of blowby gases entering a mixed-phase hydrazine

fuel system. Any thermal runaway of the liquid hydrazine present in a fuel line is almost certainly initiated in the gas phase of a mixed phase system. As a result, only gas-phase reactions were considered in this study.

The typical constituents of blowby gases as described in a pyrovalve handbook currently being written at WSTF[20] were used as initial reagents, along with hydrazine, for this project. Although the molar ratio of the blowby gases to fuel vapor present in the line is unknown, an attempt was made to ascertain reasonable initial conditions for homogenous gas-phase chemical kinetics modeling. Due to the fact that the blowby gases measured indicate a very high percentage of hydrogen in the gas, a 1:1 ratio of H_2 to N_2H_4 was used as a starting point to begin examining the effect of blowby gases on the rate of hydrazine decomposition. This ratio was chosen because the presence of a stoichiometric amount of H_2 can change the exothermicity and products of hydrazine decomposition by shifting the overall decomposition of hydrazine from R1 or R2 to R3, below.

$$N_2H_4 + H_2 \rightarrow 2\ NH_3 \qquad \Delta H_r = -187.2\ \text{kJ/mol}\ N_2H_4 \qquad \text{(R3)}$$

Several assumptions were made in carrying out this research. As mentioned above, a 1:1 stoichiometry of hydrogen to hydrazine was assumed. Additionally, to begin calculations, some thought was given as to what gas-phase species would be present near the valve at actuation. The ullage gas used in the fuel systems is helium, and it is prudent to assume if bubbles form in the fuel line, they will consist principally of helium saturated with hydrazine. At the equilibrium fuel temperature measured in an experiment prior to a destructive event initiated by a pyrovalve, the vapor pressure of hydrazine relative to the total pressure in the system (80 p.s.i.) would result in helium bubbles containing slightly under 3% hydrazine. The equilibrium fuel temperature in this experiment was below the temperature range in which several of the most important reactions in the decomposition mechanism are known. As a result, the baseline temperature decided upon for the calculations was 600 K, roughly 300 K higher than the measured temperature in the experiment cited. The rate expression for the initiation reaction for hydrazine decomposition (without the presence of blowby gases, which can change the initiation step for the mechanism) is known with a fair degree of certainty at this temperature. Three percent hydrazine in an inert bath gas at 600 K and 10 atm. was used as the baseline case.

Unfortunately, many of the key reactions in the decomposition of hydrazine are in fall-off in this temperature and pressure region, and their rate expressions have only been calculated in an N_2 bath gas. Extrapolating beyond the temperature and/or pressure region of a reaction exhibiting fall-off behavior is inadvisable, as is making assumptions as to the collider efficiency of various bath gases in a fall-off region. Due to these considerations, all calculations were performed with N_2 as the bath gas. To more properly model the behavior of the system in He will require QRRK calculations to determine the rate expressions in He bath gas for the reactions in fall-off. It should be noted that performing the modeling in N_2, rather than He, should result in a lower overall temperature rise, as well as a shallower slope in the temperature curve than what would result in He, due to N_2's greater heat capacity.

RESULTS

Decomposition With and Without Molecular Hydrogen Initially Present

The results of calculations of the decomposition of 3% N_2H_4 in N_2 at 600 K and 10 atm. indicate the compound is extremely stable at that temperature and pressure. Traditionally, the homogenous gas-phase chemical kinetic codes utilized are used to evaluate situations involving relatively rapid reactions, so the absolute value of the half-life of hydrazine at the conditions stated is somewhat questionable. Nevertheless, the calculated half-life of hydrazine at the baseline conditions was on the order of 10^6 seconds. Essentially, it is infinitely stable. The decay curve for hydrazine is shown in Figure 1.

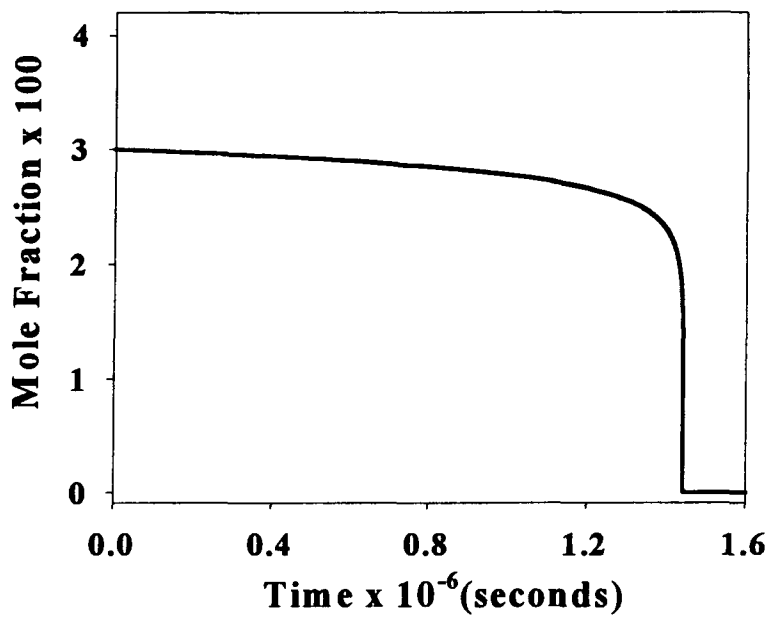


Figure 1. Hydrazine Mole Fraction vs. Time for the Thermal Decomposition of Hydrazine at 600 K, 10 atm, N_2 bath gas, 3% Hydrazine.

As seen in the figure, the hydrazine concentration remains fairly stable for a long period of time, then enters a period of rapid decrease. This induction period is indicative of a very gradual build up of reactive radicals in the gas mixture, until some critical concentration is reached, enabling a rapid decomposition of hydrazine, with concomitant rapid increase in heat release rate and temperature. A similar decay curve results from the decomposition of hydrazine in a 1:1 mixture of hydrazine and hydrogen gas, with a very substantial and prominent difference in the half-life of hydrazine. For both of these scenarios, the initiation step of the decomposition remains the same: the breakage of the N-N bond in hydrazine. What is of particular interest, and somewhat surprising, is the extent to which molecular hydrogen in the initial mixture accelerates the decomposition of hydrazine. The change in hydrazine half-life from the baseline case (i.e., no H_2 initially present) to the case where a 1:1 H_2:N_2H_4 starting ratio exists is *five orders of magnitude*.

The first solid symbols in Figure 2 represent the values obtained with molecular hydrogen as a reagent. All data in Figure 2 was calculated assuming a 1:1 H_2:N_2H_4 ratio at 600 K and 10 atm. The dramatic change in the thermal stability of hydrazine in the presence of molecular hydrogen is extremely important. The finding must be considered in the context of the possibility of a thermal runaway situation. Hydrogen gas is a final product of N_2H_4 decomposition as shown in R1 and R2; its presence as a reagent dramatically increases the rate of hydrazine decomposition. In practical terms, the meaning of this feature of hydrazine chemistry is clear: once started, the thermal decomposition of additional hydrazine present in a fuel line would be accelerated by one of the products of that decomposition. Such behavior within a neat chemical system can easily lead to thermal runaway once the process is initiated.

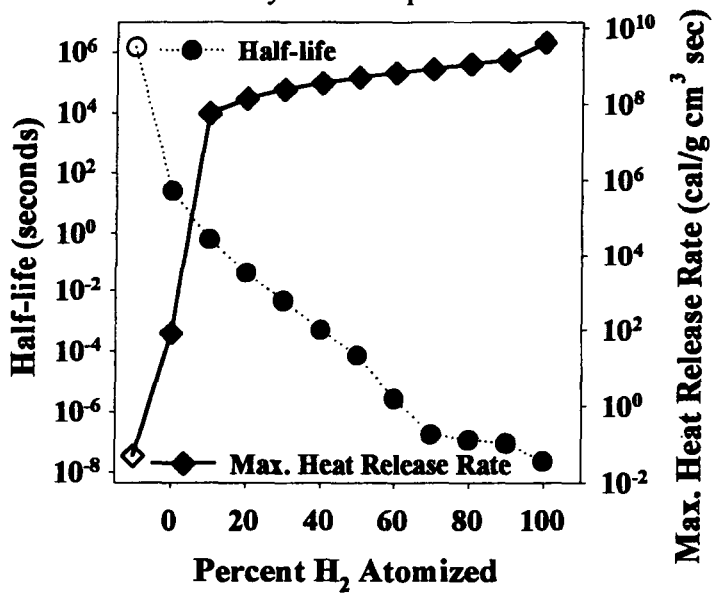
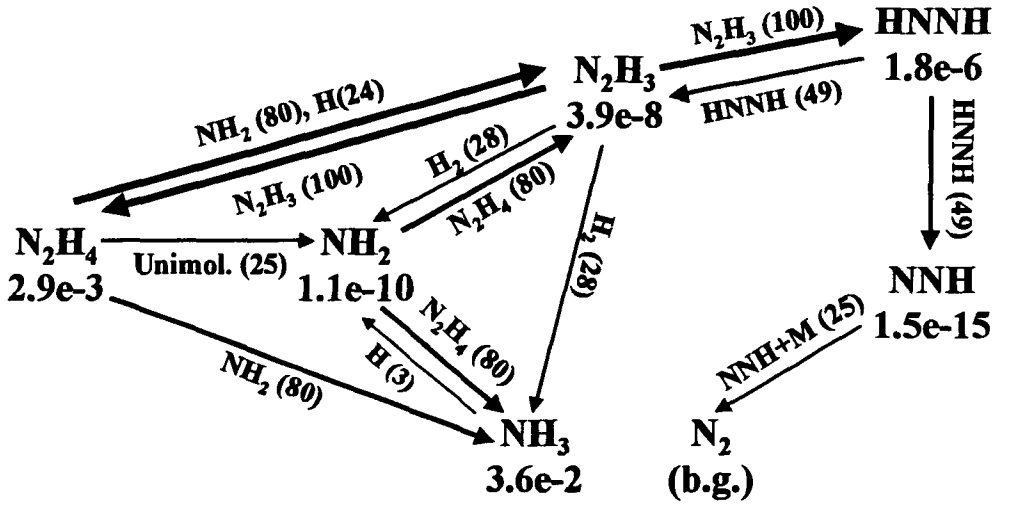


Figure 2. Plot of Hydrazine Half-life and Maximum Heat Release Rate vs. Percent of H_2 Atomized. The hollow symbols represent the values when no H_2 is initially present.

The chemical process by which H_2 gas so profoundly accelerates the destruction of N_2H_4 is primarily due to one elementary step in the mechanism. As stated earlier, without H_2 as a reagent, the reverse of Step #1 in Table 1 initiates decomposition. This N-N bond breakage produces two radicals. At 600 K this reaction is extremely slow. That same reaction is the initiation step for hydrazine decomposition when H_2 is present. However, the reverse of Step #35 in Table 1 is an extremely fast reaction that is both exothermic and chain propagating. Thus, a rapid propagation step is activated in the mechanism early on in the decay process when H_2 is present initially, leading to a more rapid buildup of radicals and subsequently shorter half-life. The NH_2 radicals produced by reversing Step #35 in turn attack hydrazine itself, a propagation step independent of H_2 presence. These differences in behavior can be visualized by examining the pathway

diagrams in Figures 3 and 4.



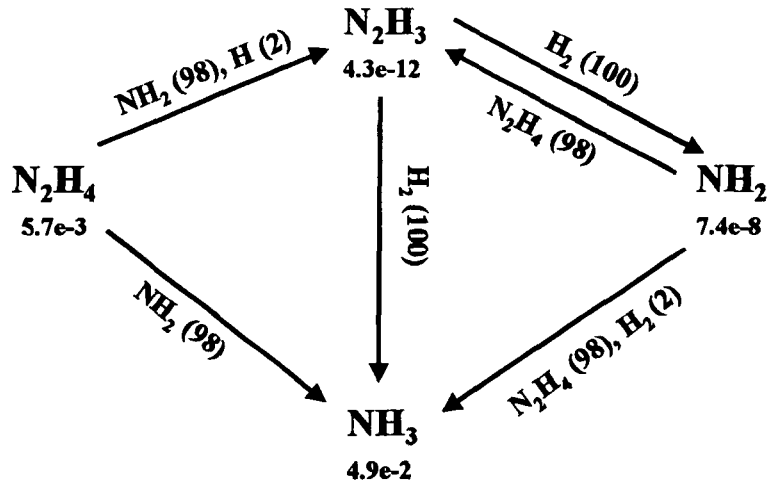
Time at 1.4e6 sec (max. heat release), 100 = 9.4e-9 mol/cm³ sec

Figure 3. Pathway Diagram for N_2H_4 Decomposition at Time of Maximum Heat Release Rate. Initial Conditions of 3% N_2H_4 in N_2, 600 K, 10 atm.

Figure 3 shows the pathway diagram for hydrazine decomposition when H_2 is not an initial reagent. The time at which this diagram is accurate is the time of maximum heat release rate. The values directly underneath the species in the diagram represent the mole fractions of the species at that time. N_2 does not have a numerical value for the concentration because it is the bath gas for all the calculations, hence, its concentration is relatively unimportant. For both Figures 3 and 4, the rates of the various reactions shown are scaled to a value of 100, and the absolute rate of the reaction against which the others are normalized is given.

The pathway diagram presented as Figure 3 has several interesting features. Even at the time of maximum heat release rate, there is a considerable back reaction of N_2H_3 with itself to regenerate hydrazine. The reactions that result in a net destruction of hydrazine at this point in time consist of the reactions of the NH_2 and H radicals with hydrazine. Also of interest is the fact that the formation of two products of decomposition, ammonia and nitrogen, are represented. The nitrogen produced is reached only through one sequence of reactions, while the ammonia is produced via two reactions, one of which directly consumes hydrazine. This diagram is indicative of the overall stoichiometry of R1.

Figure 4 presents the pathway diagram for hydrazine decomposition when an equamolar amount of H_2 is initially present. The chemical pathways leading to the destruction of N_2H_4 are considerably simpler in this case, due to the dominance of the $H_2+N_2H_3=NH_3+NH_2$ reaction and subsequent reaction of the NH_2 radical produced with hydrazine. Also, there are no reactions producing hydrazine present at the time of maximum heat release, which results in a steeper slope in the N_2H_4 concentration curve at that point.



Time at 25.52 sec (max. heat release), 100 = 9.95e-6 mol/cm³ sec

Figure 4. Pathway Diagram for N_2H_4 Decomposition at the Time of Maximum Heat Release Rate. Initial Conditions of 3% N_2H_4 and 3% H_2 in N_2 at 600 K, 10 atm.

The decomposition of hydrazine in the presence of a stoichiometric amount of molecular hydrogen is accomplished through a much "cleaner" process; fewer intermediate species are produced in any significant amount during the decomposition. Additionally, the sequence of reactions leading to the production of N_2 gas under these conditions is suppressed, due to the rapid consumption of N_2H_3 radical by H_2. Because N_2H_3 is quickly destroyed through reaction with molecular hydrogen, the formation of HNNH and subsequent reactions to yield nitrogen are negligible. The overall stoichiometry for this condition is represented by R3.

Decomposition in the Presence of Molecular and Atomic Blowby Species

There is considerable uncertainty about the actual composition of the blowby gas as it reaches the fuel line. This uncertainty arises as a result of the measurement technique currently employed. The residual gas analyzer used to measure the total mass and relative concentrations of the gas-phase species in the blowby is not an instantaneous technique – therefore, only stable species are measured. Any radicals reaching the evacuated simulated fuel line are long since converted to molecular species prior to the time of the actual measurements. Calculations were performed wherein varying amounts of the molecular hydrogen is present as atomic hydrogen in the initial mixture while maintaining the same overall stoichiometry resulting in R3. The results of these calculations are shown in Figure 2, which presents the half-life and maximum heat release rate vs. percent atomization of hydrogen in a 1:1 mixture of H_2:N_2H_4.

Examination of Figure 2 indicates a considerable decrease in the half-life of N_2H_4 and increase in the maximum heat release rate when the initial conditions include 10% of the hydrogen existing as H atom as compared to all the hydrogen existing as the molecular species. This is expected, due to the attack of the H atom on N_2H_4. That reaction generates N_2H_3 radical, which can then rapidly react with the molecular

hydrogen present as discussed above. The fact that the half-life curve in Figure 2 shows some tendency toward leveling off as the percentage of hydrogen atomized is increased is due to the reverse of Step #10 in the mechanism. This chain termination step becomes increasingly important as the atomic hydrogen concentration increases, which limits the rate at which the N_2H_4 half-life decreases.

The rate of maximum heat release vs. percentage of molecular hydrogen atomized shows a steady increase after 10% atomization is assumed, as shown in Figure 2. This fact is not surprising, since the reactions of H atom with N_2H_4 are exothermic, and very rapid. Results of calculations for the lower percentages of hydrogen atomization produced heat release rate curves with very steep initial slopes which then level off until a secondary heat release peak occurs. This secondary peak in the heat release rate occurs simultaneously with a sharp drop in the concentration of hydrazine. Above 60% atomization of the hydrogen, this feature of the heat release rate and N_2H_4 concentration curves disappears.

A major concern in conducting this study is the fact that the species that actually contact the fuel or fuel vapor present are, in fact, unknown. It is rather unlikely, but not impossible, that the molecular species measured that have weaker bonds are reaching the fuel as wholly atomized species. Likewise, it is possible, but not likely, that the blowby gases reach the fuel as they are measured, consisting only of molecular species. The probability is quite high that some mixture of molecular and atomic species reaches the fuel, rather than either extreme. Hydrogen gas is known to heat up when forced through a small orifice in going from a region of higher pressure to one of lower pressure at most temperatures, due to its Joule-Thompson coefficient.[21] This process alone could produce some atomic hydrogen in the mixture of combustion products that reaches the fuel.

Representative calculations using the inclusive mechanism and all the gaseous species measured in the blowby gas were performed. Three conditions were used: the first with the assumption that the blowby gases exist only as molecular species, the second with the assumption that 10% of the species likely to be atomized (based on bond energies) reach the fuel in the atomic state, and thirdly, that 50% of the species likely to atomize will have done so at the time of contact with the gas-phase hydrazine. A 1:1 H_2:N_2H_4 stoichiometry was maintained for all three cases, with the concentrations of the other blowby species scaled according to their mole fractions as measured.

The results of the calculations of all three cases indicate that the other blowby species contribute little to the acceleration of hydrazine decomposition. In the first case (no atomization), the decrease in N_2H_4 half-life was slightly less than that seen from assuming the blowby gas was pure H_2. Both cases of atomization resulted in slight increases in the accelerating effect on the decomposition of hydrazine. However, the changes in N_2H_4 half-life as calculated with pure H_2 added vs. all blowby species included as compared to the pure N_2H_4 in an inert bath gas were minor.

CONCLUSIONS

Hydrazine is resistant to thermal decomposition at low temperature (600 K) due to the slow rate of the initiation reaction. The calculations performed for this study, however, indicate that a readily accessible means of decomposition initiation exists under

conditions likely to occur in a fuel line due to blowby from pyrovalves. Equally important, the research revealed a chemical mechanism for propagation of hydrazine decomposition throughout a fuel line due to the accelerating effects of molecular hydrogen, which is a decomposition product, on the decomposition process itself. This aspect of hydrazine decomposition chemistry has not been previously noted in the literature. Although physical processes would have effects and must be considered in any thermal runaway scenario, the chemistry of hydrazine itself would play a key role in such an event.

The results of this investigation into hydrazine chemistry raises some technical issues that need to be addressed to fully understand the conditions under which a destructive decomposition of N_2H_4 can occur in "real life" situations. Clearly, the rate expressions for key fall-off reactions need to be revised to more accurately reflect conditions in spacecraft fuel lines, i.e., QRRK calculations should be performed to get smooth-fit pressure dependent rate expressions in He.

Another deficiency with the current chemical mechanism relating to the rate expressions for the fall-off reactions is their lack of pressure dependency as used. The reference from which those expressions were taken did not include true fall-off forms, rather, the published expressions used were presented for three constant pressure cases. Therefore, the rate coefficients for the reactions in fall-off are not entirely valid as the decomposition proceeds and the pressure of the system changes. The rate expressions used in this work were those which most closely corresponded to what is presumed to exist in the simulated fuel line in the experiments cited earlier.

Ideally, experimental work to validate the effect of molecular hydrogen on N_2H_4 decomposition should be performed. Experiments involving a multiphase hydrazine system with the inclusion of H_2 into the initial mixture should be completed. Accelerating Rate Calorimetry (ARC) would be a particularly useful technique for such a study. Liquid hydrazine could be placed into a bomb, with a small amount of He above the liquid, thus generating a multiphase system. Data could then be taken as the system is gradually heated until thermal runaway begins. The experiment could then be repeated with hydrogen gas added to the He in an amount close to 1:1 stoichiometry with the known vapor pressure of hydrazine at the initial temperature. The time/temperature at which thermal runaway starts for the two conditions could then be established, and any differences observed could provide some experimental validation of the results of this work. Although ARC does not give direct information about the concentrations of species as decomposition proceeds, the gross properties of the system itself that are measured in this type of experiment, and any changes resulting from the addition of molecular H_2, could provide valuable information.

Additional experimental studies to validate the computational results obtained using the current chemical kinetic mechanism should be performed via shock-tube or high-temperature photochemistry (HTP) research of hydrazine decomposition, and hydrazine/hydrogen mixture behavior. Shock-tube work is generally limited to fairly high temperatures (usually exceeding 1500 K), but it would be useful to quantitate the decomposition behavior under those conditions as a check on the ability of the mechanism to predict hydrazine decomposition rates in a variety of conditions. HTP

studies can be run at considerably lower temperatures, and can include the ability to generate radical species (such as H atom) in situ to ascertain their effects on hydrazine decomposition.

The determination of the amount and composition of blowby gases as performed with the current experimental apparatus at WSTF has proven useful in this research. More rapid determination of the composition of the gases that provided real-time values as the blowby gases escape the combustion chamber of the valve would be invaluable for the purposes of input into a chemical model. It should be noted that experiments providing real time measurements of blowby gases would undoubtedly prove to be extremely challenging due to the exceptionally short duration of the events being measured, and the need to measure multiple transient species simultaneously. Other system measurements that would prove helpful in further development of this modeling effort could include studies of He solubility in hydrazine over a wide temperature range, and a window in a simulated fuel line to observe any bubbles that form prior to, or after, firing a pyrovalve so as to obtain a reasonably reliable measure of the relationship of blowby mass to fuel vapors adjacent to the valve.

A complete, detailed computational model of the initiation and propagation of the destructive decomposition of hydrazine in a spacecraft fuel line has not yet been developed. However, it may be possible to devise a less-sophisticated model that could be utilized in determining the maximum amount of blowby that could safely be introduced into a fuel system for different temperatures. Such a model would have to include heat transfer effects, and the safe upper limit for the amount of blowby would likely be established by looking at the heat release rate and total heat release calculated from the chemical kinetics and their relationship to overall heat transfer within the system. Undoubtedly, there is some lower limit to blowby mass that will result in a locally quenched reaction, rather than an uncontrolled decomposition of the fuel, and modeling may be a method for determining that limit within a reasonable margin of error.

The modeling work that was carried out this summer provides some clues as to what contributed to the destruction of a simulated fuel line observed in WSTF experiments. Chemical kinetics modeling provides insight into the detailed chemistry underlying the behavior of very complex physical and chemical systems. Although this work was specific to a particular situation, the techniques can be applied to other fuels, and/or other blowby species produced by different pyrotechnic materials as a means of screening for unanticipated hazards due to the chemistry unique to a given system.

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