SACRAMENTO PLANT

INVESTIGATIONS OF THE MECHANISMS
OF DECOMPOSITION, COMBUSTION, AND DETONATION
OF SOLIDS

Report No. 0372-01-20Q

January 1965

COPY 7 OF 3

HARD COPY  $1.00
MICROFICHE  $0.50

AEROJET-GENERAL CORPORATION
SACRAMENTO, CALIFORNIA

ARCHIVE COPY
INVESTIGATIONS OF THE MECHANISMS
OF DECOMPOSITION, COMBUSTION, AND DETONATION
OF SOLIDS

A Report to
Director of Aeronautical Sciences
Air Force Office of Aerospace Research

CONTRACT AF 49(638)-851
OSR Project No. 9750, Task 37501
ARPA Order No. 24-60, Project No. 4759

Report No. 0372-01-20Q January 1965
This is the twentieth quarterly Technical Operating Report submitted in partial fulfillment of the contract. It covers the period 1 October through 31 December 1964.

L. J. Rosen, Assistant Manager
Propellant Research Division
Solid Rocket Operations
ABSTRACT

The overall stoichiometry of the NH$_3$-N$_2$O counter-flow diffusion flame has been determined from mass spectrographic analyses of the reaction products. The exothermicity of this flame reaction is governed by the reaction

\[ \text{NH}_3 + \text{N}_2\text{O} \rightarrow \frac{1}{2}\text{H}_2 + \frac{3}{2}\text{H}_2 + \text{H}_2\text{O} \]

The volumetric reaction rate ($\dot{N}_{\text{fu, max}}$) and heat release rate ($\dot{q}_{\text{max}}$) for this reaction are $1.95 \text{g/cm}^3\text{-sec}$ and $7.6 \times 10^3 \text{ cal/cm}^3\text{-sec}$, respectively.
I. **INTRODUCTION**

The objective of the research being conducted under this contract, funded by the Advanced Research Projects Agency, is to obtain a better understanding of the mechanisms of combustion, decomposition, and detonation of solids. Current investigations are concerned with the gas-phase reactions associated with the combustion of composite solid propellants and their relationships to the energy transport processes near the solid-propellant surface.

II. **TECHNICAL STATUS**

A. **SUMMARY OF PREVIOUS WORK**

Apparent flame strength measurements were made on ammonia-nitric oxide and ammonia-nitrous oxide flames in the opposed-jet reactor at pressures ranging from 100 to 745 torr. The pressure dependencies of the apparent flame strengths gave overall reaction orders of 1.56 and 2.0 for \( \text{NH}_3-\text{NO} \) and \( \text{NH}_3-\text{N}_2\text{O} \) counter-flow diffusion flames, respectively.

The overall stoichiometry of the \( \text{NH}_3-\text{NO} \) flame reaction was deduced from mass spectrographic data and opposed-jet reaction parameters. The stoichiometry can be represented by the equation

\[
1.5\text{NH}_3 + \text{NO} \rightarrow 1.25\text{N}_2 + 1.25\text{H}_2 + \text{H}_2\text{O}.
\]

The volumetric reaction rate \( \dot{\dot{m}}_{\text{V,\max}} \) for this flame reaction was computed, using Spalding's analysis, to be \( 2.93 \text{ gm/cm}^3\text{-sec} \) at 1 atmosphere pressure. This corresponds to a volumetric heat release rate of \( 7.22 \times 10^3 \text{ cal/cm}^3\text{-sec} \).
B. CURRENT AND PLANNED WORK

The gas-phase reactions which are believed to occur above the surface of burning composite propellants containing ammonium perchlorate (Reference 1) are being investigated. Current experimental studies are concerned with the overall stoichiometry of the counter-flow diffusion flame between ammonia and nitrous oxide. These flames are being investigated by means of the opposed-jet technique, which has been described previously (References 2 and 3).

1. **Combustion of Ammonia with Nitrous-Oxide**

Experimental studies are in progress on the determination of the stoichiometry and exothermicity of the ammonia-nitrous oxide diffusion flame in the immediate region of flame extinguishment. The results of mass spectrographic analyses of representative samples of reaction products are presented in Figure 1. The samples were taken downstream from the flames and the sampling techniques are such that the values for \( \text{H}_2\text{O} \) concentration are inaccurate. This presents no problem since the data indicate that essentially all of the oxygen in the reaction products appears in the water.

The data indicate that unusually large amounts of unreacted ammonia passed through the reaction zone of these flames. This finding was unexpected, since this phenomenon was not observed in other counter-flow diffusion flames between ammonia and oxidants such as \( \text{O}_2 \), \( \text{Cl}_2 \) and \( \text{NO} \). Also burning velocity measurements on binary mixtures of \( \text{NH}_3 \) with \( \text{N}_2\text{O} \) give no indication of any unusual behavior which might distinguish this flame from those between \( \text{NH}_3 \) and the oxidants mentioned above. The only unusual feature of the \( \text{NH}_3-\text{N}_2\text{O} \) counter-flow diffusion flame that distinguished it from those studied previously is that the flame had a bell shape rather
than the usual flat disc shape. Furthermore, the flame extended downward from the mouth of the oxidant jet rather than remaining suspended between the two jets as was normally observed for counter-flow flames. Whether or not these phenomena have any bearing or effect on the nature of the reaction zone, and consequently, on the passage of NH$_3$ through it, the fact remains that the analytical results are in agreement with the results obtained for the fuel/oxidant ratio as determined from reaction parameters in apparent flame strength (AFS) measurements (Reference 4). The average value of the fuel/oxidant ratio deduced from the H$_2$/N$_2$ and NH$_3$/N$_2$ ratios listed in Figure 1 is 1.75 which agrees with the value of 1.74 determined from AFS measurements (Reference 4). On the basis of these results and the data listed in Figure 1. The complete reaction is best represented by the equation

$$1.75\text{NH}_3 + \text{N}_2\text{O} \rightarrow 0.5\text{H}_2 + 1.5\text{N}_2 + \text{H}_2\text{O} + 0.75\text{NH}_3. \quad (1)$$

However, subtracting out the unreacted NH$_3$ leaves an overall stoichiometry for the NH$_3$-N$_2$O counter-flow flame that can be represented by the sum of equations (2) and (3).

$$\text{NH}_3 + 1.5\text{N}_2\text{O} \rightarrow 2\text{N}_2 + 1.5\text{H}_2\text{O} \quad (2)$$

$$0.5\text{NH}_3 \rightarrow 0.25\text{N}_2 + 0.75\text{H}_2 \quad (3)$$

These equations (1, 2, and 3) indicate that the stoichiometric proportion (1 mole) of NH$_3$ was oxidized to the expected products, excess NH$_3$ (0.5 mole) was decomposed into N$_2$ and H$_2$, and finally, that 0.75 mole of NH$_3$ did not react. Thus, the exothermicity of the flame reaction is governed by the overall reaction

$$\text{NH}_3 + \text{N}_2\text{O} \rightarrow \frac{1}{2}\text{H}_2 + \frac{3}{2}\text{N}_2 + \text{H}_2\text{O} \quad (4)$$
with a corresponding $\Delta H = -3898$ Cal./gmNH$_3$.

The volumetric rate of reaction of ammonia for reaction (4) was calculated on the basis of Spadling's analysis of opposed-jet flames (Reference 5) by the expression

$$N_{fu,\max}'''' = \frac{\rho_{\infty} U_{\text{ext}} \rho_{fu}}{\rho_{\infty}} \frac{M_{fu}}{2 \Psi_{st} f_{st}}$$  \hspace{1cm} (5)$$

where

- $N_{fu,\max}''''$ = the maximum volumetric rate of consumption of fuel (g/cm$^3$-sec)
- $\rho_{\infty}$ = density of the fuel
- $\rho/\rho_{\infty}$ = fractional density of the fuel in the local mixture (0.33)
- $\rho_{\infty} U_{\text{ext}}$ = APS at 1 atmosphere (laminar flow) = 2.35 gr/cm$^2$-sec
- $D$ = jet diameter (0.77 cm)
- $M_{fu,\infty}$ = mass fraction of fuel in the fuel stream = 0.57
- $f_{st}$ = stoichiometric mass fraction of fuel in the local mixture = 0.41
- $\Omega_{st}$ = a dimensionless function of $f$ indicative of the burning rate in the flame = 0.938
- $\Psi_{st}$ = a dimensionless reaction-rate function = 0.25

Substitution of the above values into equation (5) yields a value for $N_{fu,\max}'''' = 1.95$ gm/cm$^3$-sec for the NH$_3$-N$_2$O flame at 1 atmosphere. This value corresponds to a volumetric heat release rate ($q_{\max}''''$) of $7.6 \times 10^3$ cal/cm$^3$-sec.

2. **Theoretical Studies**

A theoretical treatment of extinction phenomena in opposed-jet diffusion flames has been developed which differs from that given by Spalding (Reference 5). In this treatment, maximum reaction rates are determined by means of physical extinction criteria which are imposed...
on the flame process rather than previous or assumed chemical kinetic information as required by Spalding's treatment. The results of these studies will be presented in the next report.

3. Publications

A paper entitled "Surface Rate Processes and Sensitivity of Solid High Explosives", by R. F. Chaiken and F. J. Cheselske was submitted for publication in the Journal of Chemical Physics.

4. Future Work

Additional flame studies of the reaction of ammonia with nitrogen dioxide (NO₂) will be made to determine the overall stoichiometry of this flame reaction.

Theoretical studies of the theory of extinction in opposed-jet diffusion flames will be continued.

III. PROJECT PERSONNEL

During the period covered by this report, the following personnel contributed the indicated portions of their time to the program.

<table>
<thead>
<tr>
<th>Time, %</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>F. J. Cheselske, Principal Investigator</td>
</tr>
<tr>
<td>30</td>
<td>R. F. Chaiken, Technical Consultant</td>
</tr>
</tbody>
</table>
### REACTION PRODUCTS FROM AMMONIA–NITROUS OXIDE FLAMES

**MASS SPECTROGRAPHIC ANALYSES**

<table>
<thead>
<tr>
<th>Identification Number</th>
<th>Product Composition, Mole %</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N₂</td>
<td>H₂</td>
<td>H₂O(2)</td>
<td>NH₃(3)</td>
<td>N₂O(3)</td>
</tr>
<tr>
<td>FCS-1(6)</td>
<td>53.3</td>
<td>14.4</td>
<td>0.8</td>
<td>29.7</td>
<td>1.8</td>
</tr>
<tr>
<td>FCS-2(7)</td>
<td>57.1</td>
<td>16.0</td>
<td>0.8</td>
<td>26.1</td>
<td>-</td>
</tr>
<tr>
<td>FCS-3(6)</td>
<td>56.7</td>
<td>13.8</td>
<td>0.5</td>
<td>27.4</td>
<td>1.6</td>
</tr>
</tbody>
</table>

---

(1) Pressure = 450 torr

(2) These values are inaccurate due to sampling technique

(3) Unreacted

(4) Average value = 0.26

(5) Average value = 0.50 (corresponds to 0.75 moles NH₃ in products)

(6) Samples taken at extinguishment (∞U_{ext})

(7) Sample taken at 0.8 (∞U_{ext})
REFERENCES


