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VON KARMAN CENTER

SOLID PROPELLANT RESEARCH OPERATIONS OF
THE SOLID ROCKET PLANT AT THE VON KARMAN CENTER

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

~~A Report~~ To

~~DIRECTOR OF~~ AERONAUTICAL SCIENCES
AIR FORCE OFFICE OF AEROSPACE RESEARCH

15 Contract AF 49(638)-851 17
~~OSR Project No. 9750~~, Task 37501
ARPA Order ~~No~~. 24-60, Project ~~No~~. 4759
16
14 Report No. 0372-01-17 / June 1964 / Copy No.

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AEROJET-GENERAL CORPORATION
AZUSA, CALIFORNIA

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This is the seventeenth Technical Operating Report submitted in partial fulfillment of the contract. It covers the period 1 January through 31 March 1964.

AEROJET-GENERAL CORPORATION

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(Von Karman Center)

ABSTRACT

The overall stoichiometries of the ammonia-oxygen and ammonia-chlorine flame reactions h~~ave be~~en deduced from mass spectrographic analyses of the gaseous reaction products and from reaction parameters for the opposed-jet diffusion flame. The overall stoichiometry of the ammonia-oxygen flame reaction, in the pressure region of 200 to 760 torr, is best represented by the equation

$$NH_3 + [illegible]\,O_2 \longrightarrow [illegible]\,H\ [illegible]\,N_2\ [illegible]\,H_2$$

The volumetric reaction rate ($\dot{M}'''_{fu,\,max}$) and heat release rate ($\dot{q}'''_{max}$) for this reaction are 7.35 ~~g/cm^3-sec~~ and ~~2.52 x~~ 10^4 cal/cm^3 ~~-sec~~, respectively.

25 [illegible]

The overall stoichiometry of the ammonia-chlorine reaction at pressures ranging from 300 to 745 torr can be represented by

$$7\,NH_3 + 3\,Cl_2 \longrightarrow 5\,NH_4Cl + HCl + N_2$$

The volumetric rate of reaction for this equation is 3.67 g/cm^3-sec, which corresponds to a volumetric heat release rate equal to ~~9.92×10^3 cal/cm^3~~-sec.

[illegible]

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 solid-propellant surfaces.

II. TECHNICAL STATUS

A. SUMMARY OF PREVIOUS WORK

The flame reaction between ammonia and chlorine was studied by means of the opposed-jet technique. It was observed that NH_3-Cl_2 flames were considerably more difficult to establish than NH_3-O_2 and NH_3-NO_2 flames. The NH_3-Cl_2 flames were too unstable at pressures below 300 torr (nozzle diameter 0.77 cm) for accurate apparent flame strength (AFS) measurements. The results of AFS measurements indicate that the overall order for this reaction is 2.3 in the pressure range of 300 torr to 1 atmosphere. Furthermore, the apparent flame strength of this system is considerably less (~ 70% less at 1 atmosphere) than that for the NH_3-O_2 system in the same pressure range. Other workers predicted that chlorine should oxidize ammonia more rapidly than oxygen. However, at higher pressures, it is believed that chlorine may be the better oxidant.

The volumetric rate ($\dot{M}'''_{fu,\ max}$) of consumption of ammonia per unit volume for the reaction

$$6\ NH_3 + 3\ Cl_2 \longrightarrow 4\ NH_4Cl + 2\ HCl + N_2$$

was calculated, on the basis of Spalding's analysis of opposed-jet flames, to be 3.18 g/cm^3-sec at 1 atmosphere. This value corresponded to a volumetric heat release rate ($\dot{q}'''_{max}$) of 8.5 x 10^3 cal/cm^3-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 (AP) are being investigated. The proposed mechanism (Reference 1) for the deflagration of ammonium perchlorate stipulates that the overall kinetic behavior of the NH_3-$HClO_4$ redox flame reaction above the solid surface is governed by at least three competing ammonia oxidation reactions (namely, by O_2, Cl_2, and NO). Experimental and theoretical studies designed to test this proposed mechanism are currently in progress. The experimental phase of these studies is being carried out by the opposed-jet technique, which has been described previously (References 2 and 3).

1. Combustion of Ammonia with Oxygen

One aspect of the kinetics problem of determining the rate of heat release from the redox-zone of burning AP involves the determination of the stoichiometry of the pertinent gas-phase reactions. Consequently, product analyses have been carried out to determine the stoichiometry (and exothermicity) of the ammonia-oxygen flame reactions in the immediate region of flame extinguishment.

Table 1 tabulates the conditions and apparent flame strength data for opposed-jet experiments made at pressures ranging from 200 to 745 torr. Table 2 lists the results of mass spectrographic analyses of the reaction products sampled from the effluent streams of several of these ammonia-oxygen flames. The sampling and analytical techniques are such that the values for H_2O concentration are inaccurate; therefore, it is the hydrogen-nitrogen ratio that is utilized in determining the overall stoichiometry of the reaction. Such a procedure is valid since the data indicate that essentially all of the oxygen in the reaction products appears in the water. Also, the data indicate that the H_2/N_2 ratio exhibits a small pressure dependency (decreasing with increasing pressure); however, it appears that the product distribution of the NH_3-O_2 flame reaction in this pressure region is characterized by a H_2/N_2 ratio of approximately 0.5 to 0.6. This conclusion is substantiated by the results of Gaydon and Wolfhard (Reference 4) who have calculated the equilibrium compositions and temperatures of NH_3-O_2 flames for various mixture strengths. Their calculations showed that, for a fuel-oxidant ratio of 5/3, the equilibrium H_2/N_2 ratio in the flame was 0.55. This would seem to indicate that chemical equilibrium was attained in the NH_3-O_2 flames examined by means of the opposed-jet technique.

One of the chief features of the opposed-jet technique is that it provides information concerning the fuel oxidant ratio (in the flame) at extinguishment, where the reaction rate is at its maximum. This information has also been used to determine the overall stoichiometry of the NH_3-O_2 flame reaction. The results of an analysis based upon both combustion product analyses and NH_3/O_2 ratios at extinguishment are presented in Table 3. This table lists calculated coefficients for the reactants (based upon product analyses) and for the products, based upon the measured NH_3/O_2 ratios at extinguishment. An examination of the data reveals a slight disparity between the calculated and measured values of the NH_3/O_2 and H_2/N_2 ratios; however, it is clear that the overall stoichiometry of the NH_3-O_2 flame reaction is best represented by the equation

$$5\ NH_3 + 3\ O_2 \longrightarrow \frac{3}{2}\ H_2 + \frac{5}{2}\ N_2 + 6\ H_2O \qquad (1)$$

The volumetric reaction rate ($\dot{M}'''_{fu,\ max}$) calculated for this reaction was 7.35 g/cm^3-sec which corresponds to a volumetric heat release rate ($\dot{q}'''_{max}$) of 2.52 x 10^4 cal/cm^3-sec.

The stoichiometry of the NH_3-O_2 flame reaction postulated earlier in the program (Reference 1) differs from that represented by Equation (1). The previous equation,

$$2\ NH_3 + O_2 \longrightarrow H_2 + N_2 + 2\ H_2O \qquad (2)$$

was based upon thermodynamic calculations and corresponded to volumetric reaction and heat release rates of 4.81 g/cm^3-sec and 2.14 x 10^4 cal/cm^3-sec, respectively. Although the heat release rates are very nearly the same for both cases, the values of the NH_3/O_2 and H_2/N_2 ratios for the latter case do not agree with those determined experimentally.

It should be pointed out that the overall stoichiometry (Equation (1)) determined in these studies does not agree with that determined by others for the NH_3-O_2 reaction in non-flame systems. Stephens and Pease (Reference 5) have studied this reaction at temperatures ranging from 525 to 725°C using both flow and static systems. They found that the overall stoichiometry was best represented by the equation

$$4\ NH_3 + 3\ O_2 \longrightarrow 2\ N_2 + 6\ H_2O \qquad (3)$$

and that the reaction rate reached a maximum near the stoichiometric mixture (NH_3/O_2 was slightly less than 1.33). Also, it is well known that maximum flame temperatures are usually obtained with mixtures close to stoichiometric proportions and that maximum reaction rates are expected for mixtures near to this composition. In the case of the NH_3-O_2 flame in the opposed-jet, the maximum reaction rate (and heat release rate) does not occur with the stoichiometric mixture (NH_3/O_2 = 1.33) but with an NH_3/O_2 ratio of approximately 1.4. More detailed studies of this reaction in the opposed-jet flame will be required to resolve this apparent anomaly.

Combustion of Ammonia with Chlorine

The flame reaction between ammonia and chlorine has also been investigated by means of the opposed-jet technique in conjunction with a mass spectrometer in order to determine the overall stoichiometry of this reaction. Tables 4 and 5 list the reaction conditions and the results of product analyses for flame reactions carried out at pressures ranging from 300 to 745 torr. The data in Table 4 clearly indicate that the mole ratio of ammonia to chlorine, in the vicinity of flame extinguishment, is approximately 9/4 in the pressure region of 350 to 650 torr. The mole ratio values at 300 and 745 torr differ somewhat from the average value of 2.25 because of inaccurate flow rate data. The inaccuracy of these latter data is due primarily to the instability of the ammonia-chlorine flame at these pressures. On the basis of these results (Table 4), the overall stoichiometry can be represented by the equation

$$9\ NH_3 + 4\ Cl_2 \longrightarrow 5\ NH_4Cl + 3\ HCl + 2\ N_2 + 2\ H_2 \qquad (4)$$

which accounts for the measured NH_3/Cl_2 ratio of 2.25. However, the results of products analyses (Table 5) indicate that the H_2/N_2 ratio in Equation (4) is too high by a factor of about 30. An overall stoichiometry which is in better agreement with the analytical results (neglecting Run No. 41) is represented by the equation

$$7\ NH_3 + 3\ Cl_2 \longrightarrow 5\ NH_4Cl + HCl + N_2 \qquad (5)$$

The ammonia-chlorine ratio for this equation is 2.33, which lies well within the experimental error of the extinction measurements. The small amount (~ 2%) of hydrogen detected in the reaction products is probably due to incomplete reaction of the hydrogen formed in the flame as a result of thermal breakdown of NH_3 to N_2 and H_2 (Reference 4).

The volumetric rate of reaction of ammonia per unit volume for Equation (4) has been calculated on the basis of Spalding's analysis (Reference 1) of opposed-jet flames to be 3.67 g/cm^3-sec. This value corresponds to a volumetric heat release rate of $\dot{q}'''_{max}$ - 9.92 x 10^3 cal/cm^3-sec. These values and the overall stoichiometry represented by Equation (5) differ from those predicted previously (See Section II of this report).

3. Reports and Publications

Three publications describing recent research achievements are currently being prepared. The tentative titles of these papers are as follows:

"The Reactions of Ammonia with Oxygen and Chlorine in the Opposed-Jet Diffusion Flame," by F. J. Cheselske, R. F. Chaiken, and D. J. Sibbett

"Surface Rate Processes and Sensitivity of Solid High Explosives," by R. F. Chaiken and F. J. Cheselske

"Kinetics of the Decomposition of Anhydrous Perchloric Acid," by D. J. Sibbett and I. Geller

The paper by Sibbett and Geller will be submitted for publication in the very near future. A technical memorandum comprising these publications and other pertinent data, will be submitted in lieu of a final report for the year ending February 15, 1964.

4. Future Work

An examination of the reaction between ammonia and the oxides of nitrogen (N_2O, NO, and NO_2) will be initiated in order to provide information needed to define the rate-controlling processes involved in ammonium perchlorate-solid propellant combustion.

A theoretical analysis of the theory of flame strength 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.

	Time, %
F. J. Cheselske, Principal Investigator	100
R. F. Chaiken, Consultant	50
R. S. Dodds, Senior Laboratory Technician	100

REFERENCES

1. Twelfth and Thirteenth Quarterly Reports under Contract AF 49(638)-841 dated 31 December 1962 and 31 March 1963; program entitled, *Investigation of the Mechanisms of Decomposition, Combustion and Detonation of Solids.*
2. A. E. Potter and J. N. Butler, *ARS Jour.*, *29*, 54-60 (1959).
3. E. Anagnostou and A. E. Potter, "Flame Strength of Propane-Oxygen Flames at Low Pressures in Turbulent Flow," *Ninth Symposium (International) on Combustion*, Academic Press, New York 1963, pp. 1-6.
4. A. G. Gaydon and H. G. Wolfhard, *Flames, Their Structure, Radiation and Temperature*, Chapman and Hall Ltd., London, 1960, p. 297.
5. C. R. Stephens and R. N. Pease, *Jour. Amer. Chem. Soc.*, *72*, 1185 (1950).

TABLE 1

REACTION CONDITIONS FOR OPPOSED-JET FLAMES BETWEEN AMMONIA AND OXYGEN

(Nozzle Diameter = 0.77 cm)

	Identification Number							
	1-a	1-b	1-c	1-d	1-e	2	3	4-1
Reactor Pressure, torr	200	300	4[illegible]	600	745	350	450	650
NH_3 Flow Rate,* moles/min	0.124	0.282	0.[illegible]41	1.076	1.935	0.350	0.624	1.474
O_2 Flow Rate,* moles/min	0.075	0.144	0.344	0.578	1.160	0.203	0.366	0.855
Mole Ratio,* NH_3/O_2	1.65	1.96	1.86	1.86	1.67	1.72	1.71	1.72
AFS**	0.177	0.340	0.482	1.33	2.20	0.449	0.809	1.89
AFS***	0.108	0.208	0.295	0.812	1.34	0.274	0.494	1.154

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*Value at extinguishment. Average value for all experiments is 1.77.

**Apparent flame strength (laminar flow).

***Apparent flame strength (turbulent flow).

TABLE 2

REACTION PRODUCTS FROM AMMONIA-OXYGEN FLAMES

Identification Number	Pressure, Torr	Product Composition, mole %				
		N_2	H_2	H_2O	Trace Materials	H_2/N_2
	350	63.53	34.67	1.80	NO	0.545
5	450	63.90	32.76	1.01	O_2	0.513
4-1	650	60.49	28.67	11.44	NH_3	0.474

TABLE 3

STOICHIOMETRY OF THE AMMONIA-OXYGEN FLAME REACTION IN THE OPPOSED-JET AT EXTINGUISHMENT

(Nozzle Diameter = 0.77 cm)

		Based on Product Analyses							Based on NH_3/O_2 Ratio at Extinguishment						
		Moles Reactants, Calculated			Moles Products, Measured				Moles Reactants, Measured			Moles Products, Calculated			
Identification Number	Press., torr	NH_3	O_2	NH_3/O_2	H_2	N_2	H_2O*	H_2/N_2	NH_3	O_2	NH_3/O_2	H_2	N_2	H_2O	H_2/N_2
2	350	2	1.225	1.63	0.545	1.00	2.455	0.545	1.72	1.00	1.72	0.58	0.86	2.00	0.674
3	450	2	1.243	1.61	0.513	1.00	2.487	0.513	1.71	1.00	1.71	0.565	0.855	2.00	0.661
4-1	650	2	1.263	1.58	0.474	1.00	2.526	0.474	1.72	1.00	1.72	0.58	0.86	2.00	0.674
5**	200-745	--	--	--	--	--	--	--	1.77	1.00	1.77	0.655	0.885	2.00	0.740
6***	--	--	--	--	--	--	--	--	5.0	3.0	1.67	1.50	2.50	6.00	0.600

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*Obtained by difference since H_2O analyses are not accurate. Also, the data retain more decimal places than are significant.

**Based upon an average NH_3/O_2 ratio (1.77) obtained for all pressures ranging from 200 to 745 torr.

***Based upon an assumed NH_3/O_2 ratio of 5/3.

TABLE 4

REACTION CONDITIONS FOR OPPOSED-JET FLAMES BETWEEN AMMONIA AND CHLORINE

(Nozzle Diameter = 0.77 cm)

	Identification Number													
	1-a	1-b	1-c	1-d	1-e	1-f	1-g	1-h	8	9	10	40	41	44
Reactor Pressure, torr	300	350	400	450	500	550	600	745	300	650	450	450	450	300
NH_3 Flow Rate* moles/min	0.097	0.129	0.165	0.230	0.272	0.322	0.448	0.562	0.087	0.429	0.247	0.259	0.247	0.116
Cl_2 Flow Rate* moles/min	0.038	0.056	0.073	0.104	0.126	0.147	0.210	0.300	0.035	0.188	0.110	0.123	0.123	0.043
Mole Ratio**** NH_3/Cl_2	2.55	2.30	2.27	2.21	2.16	2.19	2.13	1.87	2.46	2.29	2.25	2.11	2.00	2.70
AFS (g/cm^2-sec)**	0.157	0.214	0.282	0.406	0.490	0.593	0.812	1.301	0.144	0.744	0.433	0.475	0.468	0.180
AFS (g/cm^2-sec)***	0.096	0.130	0.172	0.248	0.299	0.362	0.496	0.795	0.088	0.454	0.264	0.290	0.286	0.110

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*Value at extinguishment.

**Apparent flame strength (laminar flow).

***Apparent flame strength (turbulent flow).

****Average mole ratio = 2.25

TABLE 5

REACTION PRODUCTS FROM AMMONIA-CHLORINE FLAMES

Identification Number	Pressure, torr	N_2	H_2	HCl	Cl_2	H_2O*	NH_4Cl**	Total H_2O, NO, NO_2, NOCl*	HCl/N_2
10	450	44.72	0.50	50.35	1.71	1.7	+	2.05	1.13
40	450	41.0	2.00	55.0	trace	-	+	2.00**	1.34
41	450	35.8	2.00	62.2****	-	-	+	-	1.74
44	300	50.2	-	49.8	-	-	+	0.10***	0.99

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*The presence of H_2O and nitrogen oxides is the result of O_2 (air) contamination during the experiment.

**Quantitative data for NH_4Cl not available; + sign indicates white solid deposited in reactor was shown to be NH_4Cl.

***NO only.

****This value is uncertain because of leakage in the sample bulb.