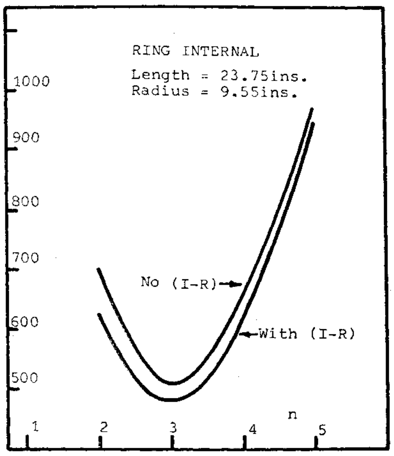

Fig. 2 Frequency spectrum showing the effect of in-plane and rotary inertia (I-R) for a shell stiffened internally with rings.

is only a small difference for even values of n. Clearly it would be of interest to extend these analyses to see whether the previous conclusions have more general validity. The frequency spectrum which is a smooth curve in the smeared case has a slight wavy pattern if the stringers are treated as discrete elements (see Fig. 3).

Thus it is shown that a one term solution with a proper choice of stiffener distribution and including the effects of in-plane and rotary inertias yields results for the natural frequencies which are in good agreement with existing experimental data and more complicated theoretical analyses using multiterm solutions (e.g., Ref. 2).

Table 5 Frequencies of a shell stiffened with 60 external stringers (m = 1)

n	Present discrete	(Ref. 2) discrete	(Ref. 2) smeared
2	666.98	736.5	736.3
3	424.89	445.3	445.1
4	297.10	304.0	303.9
5	229.56	231.8	231.8
6	197.13	197.7	197.9
7	187.83	188.2	188.6
8	194.77	196.0	196.7
9	213.33	216.1	217.0
10	240.41	245.2	246.3

The omission or inclusion of any particular effect mentioned can be studied by means of a single computer program.

The intention is to develop the program, using the information presented in this paper, for supersonic shell flutter analyses. To that end, it was decided at an early stage that the generalized aerodynamic forces would more easily be determined using the single, simple trigonometric mode chosen than from a more complex set of normal modes. Such a set could be obtained from a vibration analysis involving many degrees of freedom as in Ref. 2 but this has not been attempted here.

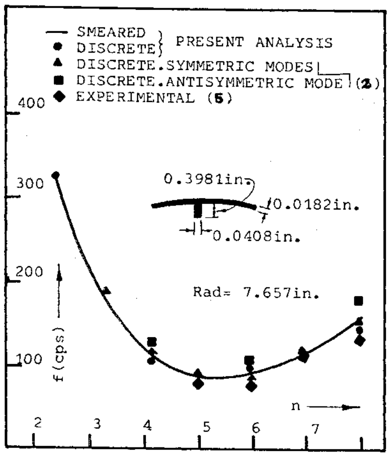

Fig. 3 Frequency spectrum, showing the effects of discrete and smeared stiffening for a shell stiffened internally with four stringers.

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Ammonium Perchlorate Combustion Analogue: Ammonia-Chlorine Dioxide Flames

J. COMBOURIEU,* G. MOREAU,† AND R. MOREAU‡
Laboratory of Chemical Kinetics,
University of Orleans-Tours, Orleans, France
AND
G. S. PEARSON§
Ministry of Technology,
Rocket Propulsion Establishment,
Westcott, Aylesbury, Buckinghamshire, England

IT is now generally accepted that ammonium perchlorate decomposes by proton transfer[1] to yield ammonia and perchloric acid

$$NH_4ClO_4 \rightleftharpoons NH_3 + HClO_4 \qquad (1)$$

At pressures above a few atmospheres, it is considered[2,3] that the combustion of solid propellents based on this oxidizer involves two flame zones. The first is a premixed flame supplied by the thermal decomposition of the ammonium perchlorate. This premixed ammonia-perchloric acid flame is markedly oxidizer rich,

$$NH_3 + HClO_4 \rightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2O + HCl + \tfrac{5}{4}O_2 \qquad (2)$$

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* Professor of Chemical Kinetics, National Centre for Scientific Research: Research Centre for the Chemistry of Combustion and High Temperatures, Orleans.

† Research Worker.

‡ Research Assistant.

§ Principal Scientific officer; presently at the British Embassy, Washington, D. C.

and is situated extremely close to the surface of the solid ammonium perchlorate. The second flame zone situated farther away from the propellent surface is a diffusion flame between the oxidizer rich products from the premixed flame and the pyrolysis products of the fuel binder. At lower pressures the premixed flame will be sufficiently far from the ammonium perchlorate crystal to allow some premixing of the pyrolyzed fuel and the diffusion flame will not be observed.

Direct attempts to study the combustion of ammonium perchlorate or of propellents are experimentally difficult.[4] Consequently attempts have been made to study related flame systems. It is apparent that studies of gaseous ammonia-perchloric acid flame systems would yield valuable insight into the combustion mechanism of ammonium perchlorate. However, such studies require 1) elevated temperature and/or reduced pressures such that the reverse of reaction (1) does not yield a condensate of ammonium perchlorate, and 2) temperatures low enough so that the perchloric acid vapor is not thermally decomposed prior to reaching the flame zone.

These two conditions tend to be mutually exclusive as the vapor pressure of ammonium perchlorate is small and the thermal stability of perchloric acid is low. Studies with perchloric acid flames have thus been made with hydrogen or simple hydrocarbon fuels and these studies have established that perchloric acid is a much more active oxidizer than oxygen.[5]

Recently, it has been shown[6] that premixed flames of methane with perchloric acid or with chlorine dioxide have a common flame mechanism. Consequently, if flames of ammonia with chlorine dioxide can be stabilized they should offer the possibility of directly simulating, for the first time, the ammonium perchlorate flame system. This note describes the stabilization of such flames and presents some preliminary results.

Experimental

The flames were stabilized at pressures of 20 to 100 torr on Pyrex burners of various diameters. The gas handling system and other details were similar to those described previously.[7] It was necessary to take stringent precautions to prevent the simultaneous condensation of ammonia and chlorine in the liquid nitrogen trap downstream of the low-pressure burner otherwise violent explosions, presumably due to the presence of nitrogen trichloride, occurred when the trap warmed up to ambient temperature. Chlorine was therefore absorbed in a soda-line column and ammonia in a subsequent zeolite column before the burnt gases passed into the liquid nitrogen trap.

Burning velocities were calculated from direct photographs of the flames. Emission spectra were recorded using a Hilger Medium Quartz spectrograph with Kodak OAO plates. Exposures ranged from 25 to 45 min with a slit width of 0.2 mm.

Results

Ammonia-chlorine dioxide flames were stabilized for a range of compositions at 65 torr. The flames were yellow and frequently showed a yellow plume downstream of the reaction zone. Emission spectra of both equimolar and stoichiometric ammonia-chlorine dioxide flames show the presence of NO, OH, NH, and NO + O.

Burning velocities were found to be practically invariant of mixture composition for the range 30–70% chlorine dioxide and to have a value of 250 cm sec^{-1} relative to the unburnt gases at 20°C.

Some experiments were carried out in which ternary ammonia-chlorine dioxide-methane mixtures were studied as a means of simulating an ammonium perchlorate propellent flame. These flames had a blue-white color in the reaction zone and a lilac or yellow plume downstream of the reaction zone. Spectra were obtained of two ternary flames (one stoichiometric and one fuel-rich). The stoichiometric flame in addition to the bands characteristic of the ammonia-chlorine dioxide flames showed the presence of CN, CH, and "cool flame" bands. The fuel-rich flame (30% ClO_2–21% NH_3–49% CH_4) showed intense "cool flame" bands. The only other bands were those of OH and, faintly, of NH. In particular no NO or NO + O bands were observed in this fuel-rich flame.

Burning velocities of methane-chlorine dioxide flames to which small amounts of ammonia were added invariably decreased even when the initial mixture was oxidizer rich (70% ClO_2–30% CH_4).

Discussion

Ammonia-chlorine dioxide flames have been stabilized for mixtures containing from 30 to 70% chlorine dioxide. The close parallel to the decomposition flame of ammonium perchlorate is evident from comparison of Eqs. (2) and (3);

$$NH_3 + HClO_4 \rightarrow \tfrac{1}{2}N_2 + HCl + \tfrac{3}{2}H_2O + \tfrac{5}{4}O_2$$

$$NH_3 + ClO_2 \rightarrow \tfrac{1}{2}N_2 + HCl + H_2O + \tfrac{1}{2}O_2 \qquad (3)$$

Since it has been shown[6] that both perchloric acid and chlorine dioxide flames with methane as the fuel have the same basic mechanism, it is reasonable to assume that the properties of ammonia flames with these two oxidizers will also display many common features.

The flame spectra observed here for the binary ammonia-chlorine dioxide system cannot be directly compared to those for ammonium perchlorate as the spectra of the latter have not been reported because of the low intensity and temperature of the flame consequent on the heat required to vaporize the solid ammonium perchlorate. However, the spectra of the ternary system with methane may be compared to the spectra of ammonium perchlorate propellents[8] and to the spectra of methane-perchloric acid flames.[7] The spectra of the mixture with 51% ClO_2–22% NH_3–27% CH_4 are particularly suitable as the mixture is only slightly fuel-rich and has an equivalence ratio of 1.1, which is similar to that of "highly loaded" ammonium perchlorate propellents. The similarity of the spectra to those obtained from propellents[8] in which OH, NH, CN, and CH were dominant is clear (see also Ref. 2).

The second ternary mixture (30% ClO_2–21% NH_3–49% CH_4) is very fuel-rich. The spectra are very similar to that observed in methane-chlorine dioxide,[7] or methane-perchloric acid[5] flames, in that the most prominent feature are the "cool flame bands" attributed to the formation of excited formaldehyde molecules. The absence of the lines characteristic of the ammonia-chlorine dioxide flame even though the exposure was 50% longer indicates that selective reaction is occurring with the methane rather than with ammonia, similar to that previously observed in binary fuel mixtures with perchloric acid.[9]

The burning velocities obtained with the ammonia-chlorine dioxide flames are appreciably faster than those for ammonia-oxygen flames with the same final flame temperature. This is shown graphically in Fig. 1 in which burning velocities are included for the related systems with methane as fuel and oxygen, chlorine dioxide, or perchloric acid as oxidizer. Equivalence ratios chosen are those for the maximum burning velocity.

The invariance of the burning velocity for mixtures containing from 30 to 70% chlorine dioxide is an unusual feature, not previously observed in gas phase flame systems. Since the major factor influencing burning velocity is the flame temperature, this suggests that the flame temperature is approximately constant over this composition range. A possible explanation is that reaction does not proceed as far as the equilibrium products when an oxidizer-rich mixture

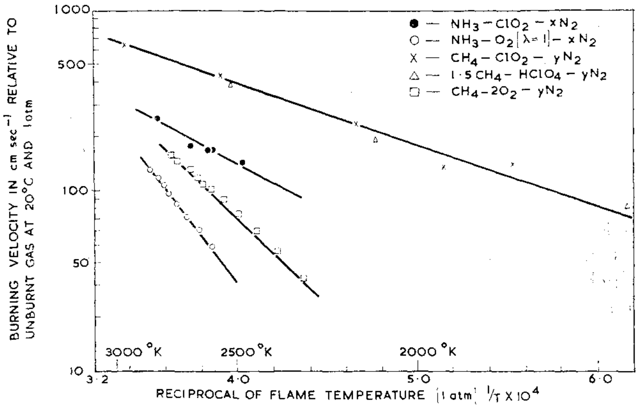

Fig. 1 Burning velocities of flames of ammonia or methane with chlorine dioxide, perchloric acid, or oxygen.

is considered. Thus, if water and chlorine are products rather than hydrogen chloride and oxygen then flame temperatures calculated at 100 torr for the composition range 30–70% ClO_2 are almost constant at 2650 ± 60°K (see Table 1).

This assumption that chlorine is favored as a product is in agreement with observations on perchloric acid flames where chlorine is observed in large excess over that expected from equilibrium considerations, especially in oxidizer-rich flames. This invariance of burning velocity of ammonia-chlorine dioxide flames is relevant to considerations of the mechanism by which catalysts are effective.[10]

The emission spectra and the burning velocity data provide strong support for the assumption that ammonia-chlorine dioxide flames display common features to ammonia-perchloric acid flames. The higher burning velocities obtained in chlorine dioxide or perchloric acid flames with methane compared to flames with ammonia suggests that the rate of reaction with ammonia is slower than that with methane. This preferential reaction with methane rather than with ammonia is strikingly shown by comparison of the burning velocities of an oxidizer rich binary mixture containing 70% ClO_2–30% CH_4 with a similar mixture containing the same ratio of ClO_2 to CH_4 along with 20% ammonia (see Table 2).

Although the theoretical temperature is only slightly affected by the addition of ammonia the burning velocity is markedly reduced.

The significance of these observations and of ignition data obtained previously[11] in relation to the combustion mechanism of ammonium perchlorate propellents is interesting. Ignition experiments with impinging jets of ammonia and perchloric acid have shown[11] that, in the temperature range studied, a surface is required for ignition to occur and that the order of decreasing ignitability under these conditions is then ammonia > isobutene > ethylene > methane. This contrasts with the results for the relative rate of reaction of ammonia and methane with chlorine dioxide, and presumably perchloric acid, described here. It is also known[2,3] that the burning rate of ammonium perchlorate propellents, especially under high pressures, is similar to that of pure ammonium perchlorate and the rate of burning in both cases is considered to be controlled by the ammonium perchlorate decomposition flame. It is therefore suggested that heterogeneous reaction involving ammonia and perchloric acid may play a particularly important role in the combustion of ammonium perchlorate propellents at high pressures and that this leads to the observed lack of influence of the fuel binder under these conditions. At lower pressures, where fuel pyrolysis products can more readily diffuse and premix with the ammonia and perchloric acid before reaction has occurred, there will be preferential attack on the fuel species and the contribution from heterogeneous reaction may be less important.

Table 1 Flame temperatures for NH_3—ClO_2 mixtures

		Temperature, °K, at 100 torr	
% ClO_2	Equivalence ratio	Equilibrium products	Cl_2 and H_2O products
23.1	2.0	2250	2250
25.0	1.8	2376	2376
27.2	1.6	2489	2489
30	1.4	2582	2582
33.3	1.2	2648	2648
37.4	1.0	2681	2675
42.9	0.8	2676	2714
50.0	0.6	2627	2714
59.9	0.4	2480	2651
75.0	0.2	2059	2466

Table 2 Burning velocities of CH_4—ClO_2 and CH_4—NH_3—ClO_2 flames

Mixture	Burning velocity, cm sec^{-1}	Theoretical flame temperature, °K
70% ClO_2 30% CH_4	460	2763
56% ClO_2 24% CH_4 20% NH_3	292	2774

Finally, the burning velocity data for equimolar ammonia-chlorine dioxide mixtures diluted with argon or nitrogen have been used to deduce an over-all activation energy using the Van Tiggelen expression.[12] The activation energy obtained is 27 kcal mole^{-1} which is in reasonable agreement with the activation energy of 32 kcal mole^{-1} obtained by Jacobs[3] for the decomposition of ammonium perchlorate under a wide range of conditions. The activation energy for ammonia-chlorine dioxide flames is appreciably less than that for ammonia-oxygen flames[12] (59 kcal mole^{-1}) and is somewhat greater than for methane-chlorine dioxide flames[6] (15 kcal mole^{-1}) which is in accordance with the faster rate of methane flames. The values for the activation energy support the present idea that at low pressures the combustion process of ammonium perchlorate propellents involve competition in the gas phase between

$$NH_3 + ClO \rightarrow NH_2 + HOCl \qquad (4)$$

and

$$RH + ClO \rightarrow R + HOCl \qquad (5)$$

where RH is a hydrocarbon fragment from the hydrocarbon binder.

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Optimum Mixing of Hypergolic Propellants in an Unlike Doublet Injector Element

John Houseman*
Jet Propulsion Laboratory, Pasadena, Calif.

Introduction

THIS communication discusses a newly found optimum mixing condition for an unlike doublet injector element with hypergolic propellants. The fluid dynamics of the impingement region of an injector element can be altered appreciably by liquid phase chemical reactions at the interface of the propellants. This effect can be used to considerable advantage to obtain better mixing of the propellants than would be possible without chemical effects. However, the extent of the liquid phase reaction must be controlled by careful selection of the injector operating conditions since too much reaction results in poor mixing of the propellants.

The unlike doublet is a common injector element in liquid rocket engines and its function is to produce a spray of well-mixed droplets of fuel and oxidizer. Typically, an unlike doublet consists of two cylindrical jets of liquid propellant that impinge on each other at an angle of from 45° to 90°. A liquid sheet is formed at 90° to the plane of the jet centerlines. With normal turbulent jets the sheet extends for only a few jet diameters and then breaks up into fine droplets. The degree of mixing is a function of several operating parameters and an optimum mixing criterion has been formulated by Rupe[1] after an extensive study of the spray produced by chemically nonreactive streams. The most uniform spray is produced when the products of fluid density, jet velocity squared, and jet diameter are equal for both streams. Even under those conditions, the spray contains an oxidizer-rich region on the side of the fuel orifice and a fuel-rich region on the side of the oxidizer orifice. It appears as if a fraction of each jet has penetrated through the impingement area to reach the other side of the main liquid sheet that is produced. This penetration effect is an accepted and well-documented facet of jet impingement. However, it has never been demonstrated experimentally with actual propellants until now.

With the advent of hypergolic propellants, another mechanism for spray formation was postulated, namely separation.

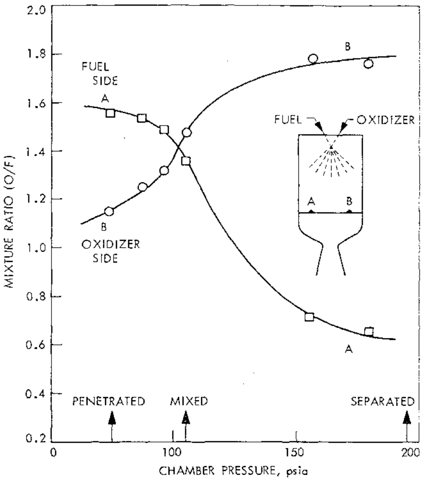

Fig. 1 **Transition from the penetrated to the separated mode of jet impingement.**

With very reactive propellants, liquid phase reactions in the impingement region of the jets can cause so much gas formation that the streams never mix but remain separated. This separation phenomenon results in an oxidizer-rich spray on the side of the oxidizer orifice and a fuel-rich spray on the side of the fuel ornifice. The gas formation in the impingement zone deflects the jets away from the impingement region. Thus, separation produces exactly the opposite effect of penetration. Evans, Stanford, and Riebling[2] have shown the relation between separation and reduced rocket engine performance. Burrows[3] and Breen et al.[4] have made photographic observations of jet separation. Tentative criteria to predict the presence or absence of jet separation have been advanced by Kushida and Houseman[5] on the basis of theoretical analysis.

The following possible mechanisms for the formation of gas in the impingement region are now envisioned:

1) The liquid phase reactions produce gaseous products.

2) The liquid phase reactions generate so much heat locally that the propellant begins to boil.[5]

3) The fuel and oxidizer jets are separated by a thin film of mixed gas. The reaction in this gas film generates a sufficient amount of heat to vaporize enough oxidizer and fuel on both sides of the film to maintain the film.[5]

A study of these combustion effects in sprays was undertaken to determine the range of applicability of nonreactive spray data to hypergolic propellant systems. An interim objective of this study is presented in this paper, namely, direct experimental data that show the existence of both the penetrated and separated mechanism of spray formation for hydrazine and nitrogen tetroxide propellants. These different mechanisms have been identified by measuring the chemical composition of the combustion gases resulting from the propellant spray. It is shown for small orifices that there is a gradual transition from penetration to separation as the flow rate and chamber pressure are increased. It is proposed that the transition zone between penetration and separation represents a new optimum mixing condition for hypergolic propellants.

Experimental Results

An unlike doublet injector element was mounted in a 3-in.-diam rocket chamber, as shown schematically in Fig. 1. A water-cooled sampling probe extends across the chamber 5 in. downstream from the jet impingement point. The probe can be traversed across the chamber and carries a sampling tip through which the combustion gases are continuously withdrawn for on-line analysis with a quadrupole mass spectrometer.

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* Member of the Technical Staff.