UNCLASSIFIED

Defense Technical Information Center
Compilation Part Notice

ADP011163

TITLE: An Experimental Examination of the Relationship between Chemiluminescent Light Emissions and Heat-release Rate Under Non-Adiabatic Conditions

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Active Control Technology for Enhanced Performance Operational Capabilities of Military Aircraft, Land Vehicles and Sea Vehicles

[Technologies des systemes a commandes actives pour l’amelioration des performances operationnelles des aeronefs militaires, des vehicules terrestres et des vehicules maritimes]

To order the complete compilation report, use: ADA395700

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:

ADP011101 thru ADP011178
An Experimental Examination of the Relationship between Chemiluminescent Light Emissions and Heat-release Rate Under Non-Adiabatic Conditions

L. C. Haber, U. Vandsburger, W. R. Saunders and V. K. Khanna
Reacting Flows Laboratory, Department of Mechanical Engineering
Virginia Tech, Blacksburg VA 24061-0328, USA

ABSTRACT

Combustion instability research has matured over the last decade and with it the need for more detailed diagnostics has increased. One main gap in the diagnostics is the ability to obtain a reliable quantitative measure of unsteady heat-release rate. In an effort to move in this direction using chemiluminescence as the measured quantity, this paper examines the formation of chemiluminescent light in premixed flames under non-adiabatic conditions. The main chemiluminescent emitters considered in the study are OH* and CH*. Experimental results for two types of burners are reported, a laminar Bunsen burner with co-flow and a ceramic honeycomb flat flame burner. The study shows that although the chemiluminescence observed in the two burners behaves very differently with respect to changes in experimental variables, the variation can be fully understood. OH* chemiluminescence is found to be a good indicator of heat-release in both burners, whereas CH* chemiluminescence is shown to be insensitive to some changes in heat-release rate. Based on the experimental results, the notion that chemiluminescence yield behaves linearly with flow-rate cannot be universally supported. The non-linear variation observed is shown to correspond to an equally non-linear variation of heat-release with flow-rate. The results of the study thus have important ramifications for the interpretation of chemiluminescence measurements in dynamic combustion environments.

1 INTRODUCTION

To truly understand the nature of combustion instabilities the ability to measure the influence of acoustic velocity and pressure perturbations on the flame heat-release rate is indispensable. The heat-release measurement capability is also important in the development of models that predict combustion instabilities. Chemiluminescence measurements have often been made to obtain some qualitative indication of the nature of the above described interaction (Samaniego et al., 1993). Quantitative heat-release rate deductions from chemiluminescence measurements have also been made but on a purely empirical basis, assuming a relationship between heat-release rate and chemiluminescence without direct verification (Langhorne, 1988).

To develop confidence in chemiluminescence as a reliable measure of heat-release rate, the relationship between the two quantities must be fully understood. Previous studies (Price et al., 1968) have not analyzed the connection between chemiluminescence and heat-release in great detail because knowledge of the reaction mechanism was very limited. The work presented here uses a detail analysis of experimental results on two very different burners to help develop the desired level of understanding of the relationship between chemiluminescence and heat-release. The study also has included a large modeling effort (Haber et al., 2000) to help provide a foundation for the analysis results presented below.

The understanding of the relationship between chemiluminescence and heat-release relies heavily on a final complete knowledge of the formation paths of chemiluminescent species. The formation chemistry of chemiluminescent species has received some recent attention (Devriendt and Peeters, 1997) but is still not fully understood. In the case of OH* the currently accepted mechanism was proposed by Krishnamahari and Broida (1961) and has only been verified indirectly by Porter et al. (1967), by Becker et al. (1977) and by Dandy and Vosen (1992).

The present study considers OH* and CH* as the main chemiluminescent species of interest. CO2 has been studied as another possible indicator of heat-release rate (Samaniego et al., 1993) but will not be discussed in this paper. OH* and CH* are the major chemiluminescence emitters in lean hydrocarbon flames, apart from the CO2 emission continuum.
The fuel used in both present burner studies is methane. Methane was chosen not only for its relatively well-known reaction mechanism but also because methane forms a large percentage of natural gas, which is used in most modern lean premixed gas turbine combustors. The use of methane gas allows conclusions drawn from the present study with respect to heat–release relationships to be more easily applied to the gas turbine combustor environment. The present report, however, does not include the study of a turbulent type flame. Since however, the chemical kinetic path of methane reaction remains the same in any combustion system, it is expected that at least qualitatively correct deductions about chemiluminescence measurement in gas turbine combustors can be made.

The experimental setup used to perform measurements in each of the burners is discussed in Section 2. Experimental results obtained from these burners are shown in Section 3. Analysis of the results with respect to heat–release rate and chemiluminescence formation paths is presented in Section 4. Conclusions and ongoing research are given in Section 5.

2 EXPERIMENTAL SETUP

Bunsen burner

The Bunsen burner used in the present study consists of a 12 mm stainless steel tube that is mounted concentrically into a long quartz chimney. The shroud around the stainless steel burner is required to protect the Bunsen burner flame from drafts. To keep the flame from extinguishing inside the quartz chimney, an annular co–flow of air is added. The co–flow is kept constant for all experiments. To assure flows of relatively low turbulence fine screens are mounted upstream in the main combustion flow as well as in the annular co–flow.

The Bunsen burner flame is such that very lean equivalence ratios could not be tested. The experiments cover a range of equivalence ratios from 0.75 to 1.1. The rich stoichiometries tested serve the purpose of elucidating chemiluminescence formation paths. Flow–rates studied cover the range of air–flow from 55 cc/sec to 75 cc/sec.

Honeycomb burner

The ceramic honeycomb burner consists of a ceramic matrix of small, 1.12 mm, square channels, that is mounted to the top of a 4 inch to 3 inch carbon steel bell–reducer. The bell reducer is used to thin the boundary layer and generate a flatter velocity profile on input to the honeycomb. The flame obtained by lighting mixture flowing through the ceramic honeycomb is essentially flat. A quartz chimney again protects the flame from drafts. Co–flow is not needed in the honeycomb burner to aid in flame stabilization.

The honeycomb burner in contrast to the Bunsen burner allows the study of very lean mixtures. The experimental study reported in the present paper varies the equivalence ratio between 0.6 and 1.1. The flow–rates studied for the honeycomb burner also have a wider range than that studied for the Bunsen burner. The flow–rates varied from an air–flow of 130 cc/sec to an air–flow of 270 cc/sec.

Optical system

To collect the chemiluminescence, a two–lens optical system coupled to a fiber–optic cable is used. Each of the lenses has a focal length of 1 inch and is made of fused silica for good ultraviolet light transmission. The fiber–optic cable as well is made of fused silica. The fiber–optic cable used for the Bunsen burner measurements has a diameter of 200μm while the fiber–optic cable used for the honeycomb burner measurements has a diameter of 1000μm. The lens system in each case was set up to collect chemiluminescence evenly across the entire area of the burner, i.e. the intensity measurement is truly a measure of the total chemiluminescence emitted by the flame.

The fiber–optic cable transmits the collected light to a 0.5 m Ebert monochrometer, where the light is filtered by wavelength. OH* measurements were performed at 308 nm and CH* measurements were performed at 431 nm. In order to allow relative comparisons between OH* and CH*, each of the voltage measurements was corrected not only for the wavelength dependent losses in the optical train but also for the spectral shapes of the radiation emitted by OH* and CH*. Several complete spectra at various experimental conditions on both burners were measured to calculate an integrating scale factor to be used in correcting the single wavelength voltage measurement for the fact that the voltage only represents a certain part of the total energy radiation by the transitions of a certain type of molecule. Upon correction of the voltage in this manner, a measure of the true chemiluminescence yield from the entire flame is obtained. Units for the corrected chemiluminescence are given as (cV–A), which stands for corrected volt–Angstroms.

3 EXPERIMENTAL RESULTS

Bunsen burner:

The results for the OH* chemiluminescence yield variation with equivalence ratio for all flow–rates studied are shown in Figure 1. The maximum for the chemiluminescence is located near stoichiometric mixture conditions. The decrease in chemiluminescence on the rich side is somewhat less steep than on the lean side. The dependence of OH* on equivalence ratio resembles that of laminar flame–speed on equivalence ratio. The shape of the curve does not appear to change significantly between flow–rates. Furthermore, each of the curves seems to be equally spaced at each equivalence ratio, suggesting a linear dependence of chemiluminescence on air–flow rate. Scaling relationships for Bunsen burner chemiluminescence are examined further in Section 4.
The CH⁺ chemiluminescence variation with equivalence ratio for all flow-rates studied is shown in Figure 2. CH⁺ behaves very differently from OH⁺. The peak for CH⁺ chemiluminescence lies on the rich side, beyond the range of the experimental conditions studied. As stoichiometric conditions are approached from the lean side, a near exponential dependence on equivalence ratio is found. CH⁺ chemiluminescence increases six-fold over the equivalence ratio range studied. OH⁺ chemiluminescence in contrast only exhibits an increase of 85%. The scaling relationship with flow-rate is not immediately clear upon examining Figure 2. If the dependence on flow-rate is linear for each equivalence ratio, the proportionality factor changes drastically in the equivalence ratio range studied.

**Honeycomb burner**

The honeycomb burner results are shown in Figure 3 and Figure 4. At an air flow-rate of 270 cc/sec, the experiment was limited to equivalence ratios below 0.925 due to the onset of a combustion instability. The variation of OH⁺ chemiluminescence yield with equivalence ratio for several air flow-rates is shown in Figure 3. Peak OH⁺ chemiluminescence for the honeycomb burner is observed near an equivalence ratio of 0.90. As the air flow-rate is increased chemiluminescent emission increases and the shape of the curve stays approximately the same. The honeycomb burner results differ significantly from those found for the Bunsen burner. The Bunsen burner OH⁺ chemiluminescence exhibited the peak yield near an equivalence ratio of 1.0. Full analysis of the results is presented in Section 4, but the fact that flame area for the honeycomb burner remains constant for all experimental conditions is bound to contribute significantly to the differences observed between the two burners.

The variation of CH⁺ chemiluminescence yield with equivalence ratio for several air flow-rates is shown in Figure 4. Peak CH⁺ chemiluminescence for the honeycomb burner is observed near an equivalence ratio of 1.00. The decline of CH⁺ emission for leaner mixtures is much steeper than the decline of emission for richer mixtures. The emission of CH⁺ chemiluminescence almost appears to be leveling off for equivalence ratios above 1.0. As the air flow-rate is increased chemiluminescent emission increases and the shape of the curve stays approximately the same with the possible exception of the data for the high air flow-rate of 270 cc/sec. The large increase in chemiluminescence may be due to the relatively large increase in flow-rate. The dependence on flow-rate, as was seen for the Bunsen burner is very equivalence ratio dependent. Whereas in the honeycomb burner the CH⁺ chemiluminescence yield for all flow-rates appears almost equal at low equivalence ratios, a drastic dependence on flow-rate is seen at higher equivalence ratios.

### 4 ANALYSIS AND DISCUSSION

The experimental results presented in Section 3 demonstrate how chemiluminescence measurements are particular to a specific burner and chemiluminescence type. The aim of the present paper is to elucidate the observed chemiluminescence trends with experimental variables in terms of associ-
ated variations in heat-release. To accomplish the analysis goal, the chemical kinetics of the chemiluminescent species and the combustion as well as other physical processes occurring in each of the burners are studied in detail. In the course of the analysis, each of the chemiluminescent species will be evaluated as a potential indicator of heat-release.

The discussion of the analysis results will benefit greatly from an introduction to the formation paths of the two types of chemiluminescence considered. The introduction focuses on chemiluminescence formation in methane combustion, although some of the conclusions are applicable for higher hydrocarbon combustion as well. A lot of the information pertaining to reactions involving precursors of chemiluminescence species was obtained by examining GRIMECH 3.0 (1999).

**Chemiluminescence formation paths**

In combustion environments \( \text{CH}^* \) is predominately formed from \( \text{C}_2\text{H} \) and atomic oxygen. The reaction was studied in detail by Devriendt and Peeters (1997) who found the reaction to have a low activation energy. The concentration of the precursor \( \text{C}_2\text{H} \) depends greatly on the concentration of \( \text{C}_2\text{H}_2 \). \( \text{C}_2\text{H} \) forming reactions have both comparatively high and low activation energies, depending on the other species participating in the reaction. The formation paths of \( \text{C}_2\text{H} \) and \( \text{CH}^* \) are illustrated in Figure 5. \( \text{C}_2\text{H}_2 \) forming reactions are not high activation energy reactions but are clearly very sensitive to the concentration of carbon radicals. The large variation of \( \text{CH}^* \) with equivalence ratio is a good indicator of this fact.

\( \text{OH}^* \) has long been thought to be the product of a reaction between \( \text{CH} \) and molecular oxygen, but recently Haber et al. (2000) have suggested that \( \text{OH}^* \) is formed by a reaction between the formyl radical (HCO) and atomic oxygen. The reaction rate constant used, similar to \( \text{CH}^* \), has a low activation energy. The formyl radical (HCO), precursor of \( \text{OH}^* \), is an important intermediate species in methane combustion because HCO-consuming reactions are generally very exothermic and contribute significantly to flame heat-release. HCO is formed primarily from \( \text{CH}_3\text{O} \). HCO-forming reactions generally have no or very low activation energies as illustrated in the reaction diagram shown in Figure 5. HCO consumption reactions however exhibit a variety of activation energies.

**Analysis of experimental results**

Researchers starting with Clark (1958) have found that all types of chemiluminescence commonly measured including \( \text{OH}^* \), \( \text{CH}^* \) and \( \text{C}_2^* \) vary linearly with Reynolds number, i.e. flow-rate. The slope of the lines varied with equivalence ratio for each of the chemiluminescence types. If one assumes that the heat of reaction per unit mass of fuel is constant with flow-rate, then the linear relationship found indicates that chemiluminescence is a good indicator of heat-release rate. Indeed, normalizing the \( \text{CH}^* \) chemi-
The Weisz reaction and the mechanisms of chain initiation and propagation are discussed. The homogeneous recombination of radicals is considered, and the formation of products is analyzed. The reaction rates are calculated for different conditions.

The diagram shows the different reaction pathways and the products formed at various temperatures. The figure illustrates the complexity of the reaction network and the interplay between the reactants and products.

The text explains how the reaction progresses over time and how various factors affect the rate of reaction. The thermal analysis is performed to determine the temperature profiles and the heat transfer coefficients.

Several parameters are considered, and their effects on the reaction are discussed. The heat of reaction is calculated for different conditions, and the results are plotted in the graph.

The normalized chemiluminescence yield as a function of equivalence ratio for the Bunsen burner is shown in the graph. The yield is calculated by dividing the chemiluminescence intensity by the fuel flow rate, and the results are normalized to a single curve. The OH* chemiluminescence results need to be further normalized by multiplying by the square root of Reynolds number. The resulting curve shows that the amount of OH* chemiluminescence per unit mass of fuel burned is lower at all equivalence ratios tested when the flow rate is increased, because the normalization required a multiplication by the square root of Reynolds number.

Several clues help in the interpretation of these results. First, as mentioned, the yield of OH* per unit mass of fuel burned is lower for all equivalence ratios including rich mixtures when the flow rate is increased. Second, a developing boundary layer scales with the square root of Reynolds number. The first clue shows that mixing phenomena are not responsible for the observed scaling because the admixture of air for rich mixtures would increase the yield of OH* chemiluminescence per unit mass of fuel burned by an effective decrease in the equivalence ratio.

The second clue points to another boundary layer dependent phenomenon, that of heat transfer. Indeed, the fine wire mesh screens are mounted less than 5 inches upstream of the burner lip. The boundary layer does not have time to develop fully by the time the flow reaches the burner lip. The result is that heat transfer from the heated stainless steel tube is enhanced for higher flow rates. The temperature increase in the incoming mixture in turn produces an increase in the flame temperature. The flame temperature increase is not equal to the increase in the incoming mix-
ture temperature due to higher heat-losses by radiation, conduction as well as product dissociation. The increase in temperature within the flame affects OH* formation detrimentally by favoring higher activation energy formyl radical (HCO) consumption reactions (see Figure 5).

Based on the above reasoning, CH* chemiluminescence should have exhibited some sensitivity to the flame temperature change. However, CH* chemiluminescence formation, as discussed above, combines high and low activation energy processes. As a consequence the flame temperature increase enhances some CH* precursor formation reactions and discourages others. The small flame temperature increase therefore is not seen to affect CH* chemiluminescence. Note that the above explanation shows that the decrease in OH* chemiluminescence per unit mass of fuel burned is related to a net decrease in temperature rise across the flame. CH* fails to show the same sensitivity to heat release.

Najm et al. (1998) also found that CH* chemiluminescence was not a good indicator of heat-release rate in methane flame environments of very high curvature, near extinction. The recommended indicator of heat-release rate based on their study is the formyl radical (HCO). As discussed above, the formyl radical is a precursor of OH* which makes OH* an indicator of formyl radical concentration and by inference a good indicator of heat-release rate, even in high flame curvature environments, near extinction.

The quality of OH* chemiluminescence as an indicator of heat-release rate can be verified further by examining the results reported for OH* chemiluminescence on the honeycomb burner. The normalization of the chemiluminescence data by the fuel flow-rate leaves a residual trend with flow-rate. A plot of normalized OH* chemiluminescence versus fuel flow-rate is shown in Figure 8 for equivalence ratios of 0.7 and 1.1. It is seen that for both equivalence ratios the amount of chemiluminescence obtained per unit mass of fuel burned is an increasing function of flow-rate. To validate OH* as an indicator of heat-release rate, as defined above, the dependence of normalized OH* chemiluminescence on flow-rate must be shown to correspond to a relative decrease in heat-losses from the flame.

An analysis of the burning process in the honeycomb burner will help elucidate the chemiluminescence formation process. The flow-rate per unit area of the honeycomb burner is very low when compared to the maximum laminar burning rate. The highest flow-rate studied corresponds to a flow-rate one third of the maximum laminar burning rate. In the honeycomb burner, the flame area is always constant and the reaction rate increases to accommodate increases in flow-rate. Closely tied to increases in reaction rate are increases in the flame temperature.

Reaction rate is an exponential function of temperature. Radiation heat-loss from the flame is a function of the flame temperature raised to the fourth power. For an overall activation temperature of 16000 K, a base temperature of 1800 K and a required increase in the reaction rate of 30%, the increase in flame temperature only has to be about 3%. A 3% increase in the flame temperature results only in a 13% increase in radiation heat-loss. The radiation heat-loss is thus relatively lower at a higher burner-
flow-rates. Note also that since the flame temperature is higher, the temperature rise through the flame is higher. The increase in OH* chemiluminescence obtained per unit mass of fuel burned thus corresponds to an increase in the heat-release per unit mass of fuel burned.

As was done for OH* chemiluminescence, CH* chemiluminescence was normalized by dividing by the fuel flow-rate. Figure 9 shows a plot of normalized CH* chemiluminescence as a function of fuel flow-rate for equivalence ratios of 0.7 and 1.1. Again, a residual trend with flow-rate can be detected for both equivalence ratios. The reaction rate increase and associated flame temperature increase appears to affect CH* and OH* chemiluminescence in similar ways. Note that in contrast to the Bunsen burner, the flame temperature increase in the honeycomb burner is not caused by an increase in the temperature of the incoming gas and thus does not exhibit a similar shift towards higher activation energy reactions. The temperature increase in the honeycomb burner is tied to the reaction rate increase necessary to support the higher flow-rate, resulting in an overall increase of the throughput of all reaction paths.

All of the identified scaling relationships and trends have important consequences for the use of chemiluminescence as a dynamic heat-release rate indicator. Assuming the variation in the flow-rate occurs on a much slower time-scale than the reaction rate, the flame will adjust itself to changes in the flow-rate very quickly. Oscillations in flow-rate can then be viewed from a quasi-steady standpoint in terms of the fluctuations in chemiluminescence these oscillations produce. The non-linear scaling relationships and trends reveal that for large oscillations in flow-rate, the oscillations in heat-release rate will show significant non-linear effects. For the honeycomb burner for example, the non-linearity appears to be quadratic in flow rate because normalization by fuel flow-rate leaves an approximately linear residual trend in the same variable.

5 CONCLUSIONS

Experimental studies of chemiluminescence were performed for two different types of non-adiabatic burners, measuring OH* and CH* chemiluminescence yield. The experiments covered a wide range of equivalence ratios and flow-rates. The results underlined the fundamental differences between the two chemiluminescent species, especially in terms of their variation with equivalence ratio.

An attempt was made to identify all major processes that affect the scaling of chemiluminescence yield with flow-rate. The traditionally accepted view that chemiluminescence yield behaves linearly with fuel flow-rate must be rejected based on the OH* chemiluminescence results in both burners. CH* chemiluminescence on the Bunsen burner was linear with flow-rate but CH* chemiluminescence on the honeycomb burner was found to exhibit similar behaviour to OH* chemiluminescence. The linear relationship with fuel-flow observed on the Bunsen burner confirms the results of the study by Najm et al. (1998) that CH* is not a good indicator of heat-release rate in all flame environments. CH* chemiluminescence fails to capture a decrease in the sensible enthalpy change of the gases through the flame. OH* chemiluminescence does capture the decrease and again further confirms the results of Najm et al. (1998) that the formyl radical and by inference OH* chemiluminescence is a good indicator of heat-release rate.

The results of the analysis, even though strictly valid only in steady combustion environments, have interesting implications for chemiluminescence measurement in dynamic combustion environments. The non-linear scaling of chemiluminescence with flow-rate for a burner may point out important non-linear processes influencing such important combustion instability characteristics as limit cycle amplitude and frequency content.

The present study represents only a small step in the direction of obtaining a quantitative measure of heat-release rate. The conclusions drawn from the experimental results above are currently being verified through a detail combustor modeling effort. The methods used in the experimental study are also going to be applied to more complex flame environments in an effort to achieve the same level of understanding for turbulent flames as for laminar flames. Finally, it is important to mention that experimental studies are currently being conducted on laminar flames in dynamic flow environments.
ACKNOWLEDGMENTS

The authors would like to acknowledge the support of Mr. Ludwig Haber by a NSF Graduate Fellowship.

REFERENCES


