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Our program is directed towards increasing understanding of combustion processes in general, as well as advancing the application of fluorine-supported combustion in areas such as propulsion and chemical lasers. Since fluorine is monovalent, combustion in fluorine is chemically much simpler than combustion in oxygen. However, in fluorine-based combustion most of the energy is initially deposited into vibration (of HF), and transfer of energy from vibrationally excited species must be considered. Experiments in H_2-F_2 flames to which very small amounts of CH_4 have been added are particularly revealing and indicate that the most likely mechanism for explaining luminescence from CH and CHF radicals in these flames is vibration-to-electronic energy transfer from highly vibrationally excited HF. C_2 emission probably results from the $CH + CH \rightarrow C_2^* + H_2$ reaction. These conclusions suggest that the ratio $I_{CH}/(I_{C_2})^{1/2}$ is a useful diagnostic for vibrationally excited HF in H_2-F_2 propulsion and laser systems. Ionization is not intrinsic to fluorine-hydrocarbon combustion, but often results from oxygen impurity in fluorine.

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Fluorine combustion systems show a variety of nonsteady behaviors, which are postulated to be due to changes in concentrations of vibrationally excited species in the system. The method of kinetic titrations has been developed to obtain stoichiometric, kinetic and mechanistic information about chemical reactions. The kinetic analysis of this method, including diffusion, has been verified by measurements on the $NO + O_3$ reaction. The $NO + F$ and $NO + F_2$ reactions have also been studied by the method.

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Introduction

Besides providing some of the most rapid and exothermic gaseous reactions known, liquid F_2 as a rocket fuel oxidizer offers the added advantages of greater density (compared to liquid oxygen) and hypergolicity, permitting multiple starts of a rocket[1,2]. Mixtures of liquid fluorine and liquid oxygen (FLOX) have been proposed in order to obtain the maximum specific impulse from fuels such as hydrocarbons and the hydrides of boron, beryllium and other metals. Fluorine can also be used to obtain a rapid, initial increase in free-radical concentration to speed hydrocarbon-air supersonic combustion that must occur in limited time. Tripropellant systems can attain very high specific impulses. For example, in Li-F_2-H_2, the large enthalpy release of the $Li+F_2$ reaction is used to accelerate very light H_2 molecules.[3] Thus, high specific impulse can be achieved at a quite moderate exhaust temperature. Interest in fluorine-containing molecules as oxidants in propellant systems has focused on compounds that provide the high heat release characteristic of fluorine reactions, but are stable liquids or solids at ambient or semicryogenic temperatures. OF_2, O_3F_2, NF_3, N_2F_4, ClF_3, and ClF_5 are some of the molecules that have been considered for this purpose.

The use of fluorine-based combustion for propulsion has recently become of particular interest in connection with SDI systems employing chemical lasers. Most lasers proposed for this purpose are based on pumping reactions using fluorine as a reactant. The use of the same oxidant for propulsion and the laser would provide a considerable weight reduction for the storage tank and associated hardware.

Flame studies

Notwithstanding their higher temperature and burning velocity, fluorine flames are intrinsically simpler than oxygen flames. This is a result of fluorine being monovalent rather than divalent. There are no species analogous to peroxides and aldehydes to complicate fluorine-based combustion. As a result, mechanisms for light emissions can be more easily established in fluorine than in oxygen-supported combustion. Additionally, for flames at low and moderate temperatures, it is usually assumed that states emitting in the visible and ultraviolet region must be formed in a single reaction (chemiluminescence). Since there are no multiple bonds to fluorine, forming compounds with bond strengths comparable to CO, there are usually fewer energetically feasible routes for producing a particular excited state in a fluorine flame than in the corresponding oxygen flame. Thus, if the same phenomenon occurs in fluorine and oxygen-supported combustion, it may be easier to understand the chemical mechanism producing the phenomenon in the fluorine case, and the same mechanism may also hold in oxygen-supported combustion. Studies of combustion in fluorine are therefore anticipated to play a key role in increasing our understanding of combustion processes.

Regardless of its potential mechanistic simplicity, fluorine combustion had been relatively little studied and even less understood at the inception of our program. The reason for this is that there are a number of experimental difficulties involved in studying fluorine flames. The most obvious of these are the high temperature, burning velocity, quenching diameter and explosion potential of these systems. In addition the corrosiveness of the HF product requires considerable attention to be paid to appropriate trapping systems and materials of construction. A final difficulty arises from difficult-to-remove oxygen impurity, often as high as 1%, in commercially available F_2. As a result, it is difficult to ascertain whether observed phenomena are intrinsic to fluorine combustion or due to oxygen impurity. In our work, highly controlled experiments on F_2-CH_4 flames were performed, some using purified fluorine, in order to obtain mechanistic information on phenomena such as ionization, luminescence and unsteady behaviors in these systems.

In order to identify the mechanisms leading to chemiluminescence from F_2-hydrocarbon flames, we have been investigating such systems by the method of very dilute flames.[4] In this technique, very low concentrations of hydrocarbons (less than 2%) are added to F_2-H_2 flames while monitoring luminescence from carbon-containing species, such as CH, C_2 and CHF. Laser-induced fluorescence of CH and CHF has recently been introduced into our experiments as a means of monitoring the ground-state concentrations of these radicals. Measurements of HF rotational temperature and photography with infrared sensitive film help to define the properties of the H_2-F_2 flames to which CH_4 is added. At very low additions of hydrocarbons, the basic flame parameters, such as flame shape and burning velocity and the concentration of H and F atoms are determined by the well-understood hydrogen-fluorine kinetics, which is not altered by small additions of hydrocarbon. Thus, the dependence of the intensity of CH, C_2 and CHF emissions can be studied as a function of the concentration of hydrocarbon radicals in the flame at constant flame parameters, and the flame parameters can be varied at constant concentrations of hydrocarbon radicals.

CH and C_2 emission are well known in hydrocarbon-O_2 combustion. However, we have shown that CH emission is an intrinsic property of hydrocarbon-F_2 combustion and is not dependent on O_2 impurity in F_2.(pub.1) In very dilute flames, CH, C_2 and CHF emissions show very different dependence on flame parameters. For example, CH and CHF intensities increase linearly with CH_4 added to the flame, while C_2 intensity shows close to a square dependence. CH and C_2 intensities peak for lean flames and decrease rapidly as the equivalence ratio of the flame increases, while CHF intensity decreases much slower with equivalence ratio. As pressure is increased, CH and C_2 intensity increases rapidly, while CHF intensity decreases.(pub. 4) These observations have been explained using a mechanism involving the following reactions for populating the emitting states:

1) $CH + HF^* \longrightarrow CH$ (A and B states) + HF

2) $CHF + HF^* \longrightarrow CHF$ (A state) + HF

3) $CH + CH \longrightarrow C_2$ (A state) + H_2

Reaction (1) is also in accord with the results of experiments performed with H_2-F_2 flames to which very small amounts of CD_4 were added. In this experiment, the observed emission was mainly CD, rather than CH. The copious formation of vibrationally excited HF in H_2-F_2 flames, combined with the propensity for this energy to be transferred to electronic energy of various species suggests possible routes for producing visible chemical lasers based on molecular electronic transitions.

The proposed mechanisms for producing the emitting species provide interesting possibilities for diagnostics in fluorine-supported combustion. From reaction (1) and (3), $I_{CH}/[CH] = I_{CH}/(I_{C_2})^{1/2}$ is proportional to the concentration of HF molecules with sufficient vibrational energy to result in electronically excited CH.(pub. 4) Since superthermally vibrationally excited HF represents wasted energy in propulsion, the latter diagnostic might be useful in the exhaust of H_2-F_2 propulsion systems to which small additions of CH_4 have been added to probe the HF vibrational distribution. It may also be of use in HF lasers, where highly vibrationally excited HF is desirable.

Oxygen was removed from F_2 by reaction with SbF_5 to concentrations below 0.02% as monitored by vacuum ultraviolet spectrophotometry.[5] The levels of ionization in flames of hydrocarbons burning in purified fluorine were below our limits of measurement, strongly indicating that chemiionization is not an intrinsic property of fluorine combustion, and that the observed ions in fluorine flames probably result from the

4) $$CH + O \longrightarrow CHO^{+} + e$$

reaction resulting from oxygen impurity.(pub, 1) This result indicates that it may be possible to operate F_2-based propulsion systems with little interference to radio transmissions resulting from ionization in the rocket exhaust.

An unexpected finding during our initial work was the observation of a wide range of non-steady behaviors in low-pressure fluorine combustion (below 1 Torr). For example, F_2-CH_4 flames, over a range of flows, burn as brief repetitious intense flashes. At other flows the system shows regimes of slow diffuse reaction, rapid luminous reaction and oscillatory luminous reaction. Except for occurring at much lower pressure and over a much shorter time scale, these behaviors are very similar to those that have been reported for several oxygen-supported combustion reactions. We have performed steady-state calculations on a simple model of the F_2-CH_4 flame which predicts multiple steady states at flows corresponding to those giving the observed oscillatory behavior. We have proposed a model to explain these nonsteady behaviors (oscillations and pulsation) that we have observed in a variety of fluorine-supported flames. This model attributes the behaviors to the flames making transitions between two states. One of these states has high concentrations of vibrationally excited HF in the presence of mostly reactants, which are inefficient quenchers of excited HF. The other state has much lower concentration of excited HF, due to the presence of polar products, which are efficient quenchers of vibrationally excited molecules.

Kinetics studies

We have shown that the equivalence points of titrations in bimolecular reactions can be defined <u>kinetically</u> as the ratio of concentrations of reactants that provide the greatest persistence of the reaction.(pub. 5) This results from the fact that only at the equivalence point do the reactants decay in a second-order fashion, while at any other ratio of concentrations the decay eventually becomes pseudo-first order. In order to obtain rate constants from kinetic titrations, detailed fitting to the shape of the titration curve is necessary. For accurate results, we have modified our numerical treatment of the shape of titration curves to include axial diffusion. The theory has been verified by good agreement with titrations of the O_3 + NO reaction, monitored by chemiluminescence at long times in a flow reactor. Kinetic titrations were also demonstrated in the NO + F and NO + F_2 systems.(pub. 3)

Conclusions

To date the overall picture that we have obtained of fluorine-supported hydrocarbon combustion is that it is quite different from oxygen-supported hydrocarbon combustion. In the former, due to the exothermicity of the chain propagating reactions and their tendency to deposit this excess energy into vibrational excitation of product HF, most of the energy of combustion is initially deposited into vibrational excitation. Thus, transfer of energy from these vibrationally excited molecules is responsible for chain branching and controls the speed of the overall reaction. In addition, vibration-to-electronic energy transfer creates many of the luminescing molecules in the flame. In contrast, in oxygen-supported combustion, the chain is chemically branching, due to the bivalent nature of oxygen, but most of the energy of the reaction is not released until fairly late, as atom and radical combination occurs.

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COMBUSTION AND FLAME 67:217-221 (1987)

Combustion of Hydrocarbons in Purified Fluorine

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Emission spectra and ionization are compared in premixed flames of CH_4 burning in commercial F_2 (0.4% O_2) with those burning in purified F_2. Oxygen impurity is reduced to below 0.02% in the purified F_2 by reaction with SbF_5. No appreciable differences exist between the spectra of flames burning in commercial and purified F_2; both are dominated by bands of CHF and CH. CH emission is thus an intrinsic property of F_2-hydrocarbon combustion. In contrast, ionization (as measured by a Langmuir probe) is reduced to an undetectable level in flames with purified F_2 and is roughly proportional to O_2 concentration in flames with unpurified F_2. Ionization is thus not an inherent property of F_2-hydrocarbon combustion.

INTRODUCTION

The reactions of fluorine are among the most rapid and exothermic reactions known. As a result, fluorine has often been proposed as the oxidizer for high-performance propulsion systems. In addition, fluorine-supported combustion has been the basis for high-intensity HF chemical lasers. However, combustion in fluorine is presently not nearly as well understood as combustion in oxygen. In fact, due to oxygen being a very common impurity in fluorine systems, it is not known whether several observed properties of fluorine flames are inherent to fluorine combustion or due to oxygen impurity. In the present work, we will compare ionization and several chemiluminescences in flames of hydrocarbons burning in commercial fluorine with those in flames burning in purified fluorine, in order to establish whether these phenomena require oxygen impurity.

The nature of the light emitted from F_2-hydrocarbon flames is very dependent upon pressure and equivalence ratio. Early workers reported either C_2 Swan bands [1] or various continua [2] as the dominant visible emission. Some clarification was achieved by Patel et al. [3], who showed that progressions of CHF overlapped the Swan bands and increased in intensity at low pressure and equivalence ratio. In many flames a strong contribution from CH (A–X) emission at 431.5 nm was also reported. However, in work by Skirrow and Wolfhard [4], on flames of hydrocarbons burning in ClF_3, it was found that while C_2 bands were always present, CH bands only appeared when O_2 was introduced into the flame [2]. Reasoning that ClF_3 and F_2 flames should be quite similar, they suggested that CH emission was not an inherent property of fluorine-hydrocarbon combustion, but rather was due to the same reaction that produced this emission in oxygen-supported flames, namely, the

$$C_2 + OH \rightarrow CO + CH^* \tag{1}$$

reaction, resulting from the approximately 1% oxygen impurity in Durie's fluorine. However, in later work on premixed CH_4–F_2 flames it was reported that CH bands invariably appeared at an earlier stage than C_2 bands [5], the opposite behavior from what is observed in oxygen combustion, thus casting some doubt on attributing the CH emission to oxygen impurity. A lack of positive correlation between oxygen impurity concentration and CH emission intensity has also been reported for both atomic [6] and molecular [5] fluorine-hydrocarbon flames. In addition, CH emission has been reported in infrared laser

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excited mixtures of [illegible] with hydrocarbons [7], a system which sho [illegible] free from oxygen impurity.

Very little work has been reported on ionization in fluorine-supported combustion. In atomic fluorine flames, ionization was found to mimic that found in oxygen-supported combustion, namely, no ions in hydrogen flames and copious ions in hydrocarbon flames [8]. Since oxygen was certainly present in these experiments, these ions could have been formed by the reaction

$$CH + O \rightarrow CHO^{+} + e, \qquad (2)$$

which is generally considered to be the major ion-forming route in lean and stoichiometric hydrocarbon–oxygen flames. However, ionization has also been reported in infrared laser-excited mixtures of SF_6 with hydrocarbons [9], a system in which there should be little oxygen contamination.

EXPERIMENTAL

Due to the very similar boiling points of F_2 (−188°C) and O_2 (−183°C) and the corrosiveness of fluorine, purification of commercial fluorine by laboratory distillation is quite difficult. Jacob and Christe have reported, however, that oxygen can be removed from fluorine by reaction with SbF_5, to form $O_2^{+}Sb_2F_{11}^{-}$ and other nonvolatile compounds. This reaction is carried out in a batch process in a Monel vessel at 200°C for 2 h. Further trap-to-trap distillation can produce extremely pure F_2 [10]. Two samples of purified fluorine were used in our experiments. One was prepared by Spectra Gases Corp., using the method of Jacob and Christe. The other was produced in our own laboratory by a similar method, in which flow of the gas through a coil cooled by liquid nitrogen was substituted for the trap-to-trap distillation. Both samples gave no evidence of the Schumann–Runge bands of O_2 at 175–195 nm (absorption spectroscopy performed on a GCA McPherson model 815 vacuum uv spectrometer), which by comparison with a 5% oxygen standard (in nitrogen) indicated oxygen concentrations of less than 0.02%.

Exploration of oxygen-free fluorine combustion also requires avoiding introduction of oxygen through air leaks or chemical reactions. Fluorine atoms are known to react with oxide surfaces to release oxygen atoms. In the present work, flames were burned in a tubular aluminum combustion chamber of 6-in. diameter and 12-in length. The chamber could be pumped to below 1.0 μm pressure, using a Welch model 1395 pump. (Charcoal and liquid nitrogen traps were employed to remove corrosive reaction products.) The leak rate of the chamber was less than 1.0 μm/min. Windows were constructed from magnesium or calcium fluoride and insulators from aluminum oxide (which rapidly forms a protective fluoride coating in a fluorine atom atmosphere). No corrosion of the insulators was noted, and it was estimated that their contribution to the oxygen concentration in the chamber (after initial surface fluorination) would be small compared to the upper limit that we have placed on the oxygen impurity in the purified F_2.

Premixed flames were burned on a 0.44-in. diameter water-cooled burner. Reagents were delivered by a Union Carbide mass flow controller (model FM4575) with appropriate flow transducers and mixed in a 9-in. section of 0.44-in. tubing. Chamber pressure was measured by a Baratron gauge calibrated against a McLeod gauge. Emission spectra were recorded with a 0.25-m Jarrell Ash monochrometer using an IP28 photomultiplier tube. Due to changing window transmission, resulting from etching and soot deposition, absolute emission intensities from similar flames were quite variable. As a result, only intensity ratios within spectra are considered in this work.

Ionization was measured with both single and double Langmuir probes constructed from 0.01-in. nickel wire. (Because it forms less volatile fluorides, nickel was found to be superior to platinum as a probe material.) The probes were held under tension by springs on both ends, and the length of the probes exposed to the flame was 0.5 in. Probes were driven by a voltage which increased linearly with time. The voltage sweep was adjustable up to 300 V, and the time for the sweep could be varied from 10 to 200 s. Currents were measured by a Keithley model 614 electrometer and current was plotted against voltage on an X–Y recorder. The sensitivity for dynamic measurements, about 10 pA, was limited by capacitive currents and leakage currents due to soot deposition. The latter could be reduced to a very low level by thorough cleaning of the insulators.

RESULTS

The most intense visible emission features of CH_4-F_2 flames burning at 1-3 Torr are the A-X transition of CHF and the 0, 0 band of the A-X transition of CH at 431.5 nm. (No appreciable emission was observed from the B state of CH.) As reported by Patel, CHF bands extend at least from 450-600 nm, due to progressions in the bending vibrations of the upper and lower states. At pressures near 3 Torr, some evidence for sharp C_2 bands superimposed on the broad CHF spectrum is obtained. At similar pressures and stoichiometry the ratios of CH to CHF intensities were comparable in flames with purified and commercial (0.4% oxygen) fluorine. Because of limited availability of the purified fluorine, quantitative intensity measurements were made with commercial fluorine. As shown in Fig. 1, the ratio of the intensity of the CH band to that of the CHF bands increases dramatically with pressure over the range 1.8-2.7 Torr at a constant equivalence ratio of 0.96. Since the only vertical collimation in the optical system was the 0.75-in. diameter window, it is unlikely that this pressure dependence was due to flame movement. At constant pressure the CH/CHF intensity ratio also increased as the equivalence ratio was decreased in the fuel-rich regime. Although we have performed few experiments at F_2-rich conditions (due to difficulties with our pump handling the excess F_2), it appears that this ratio reaches a maximum at an equivalence ratio of 0.9 ± 0.1.

In contrast to chemiluminenscence, no ionization could be observed in flames of methane or acetylene burning in purified fluorine. Single probe voltage-current curves for CH_4-F_2 flames at 1.0 Torr total pressure are shown in Fig. 2, which includes curves with oxygen added to give 1.5 and 2.5% impurity, as well as one with commercial fluorine (0.4% oxygen). Curves with purified fluorine are indistinguishable from the baseline taken in the absence of gas flows. In the flames containing oxygen, the saturation ionization currents are roughly proportional to the oxygen concentration. Also of interest are the "kinks" in the transition region of the probe characteristics shown in Fig. 2 and the almost equal saturation currents at positive and negative voltages.

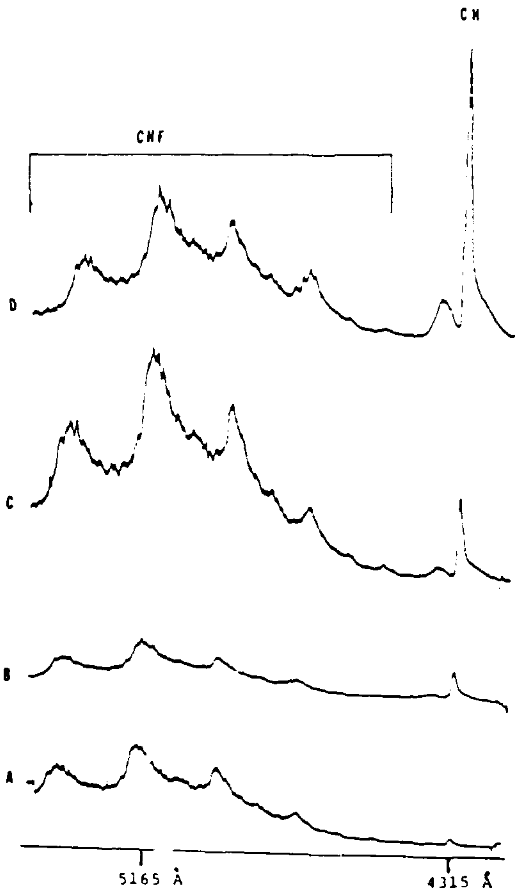

Fig. 1. Effect of pressure on emission spectrum of CH_4-F_2 flame, equivalence ratio = 0.96: (A) 1.8 Torr, (B) 2.2 Torr, (C) 2.4 Torr, (D) 2.7 Torr (evidence of C_2 bands in spectrum D).

DISCUSSION

Since the 431.5 nm band of CH is undiminished in intensity when oxygen impurity is eliminated from fluorine, this emission is an intrinsic property of fluorine-hydrocarbon combustion. The only evidence to counter this conclusion is the requirement

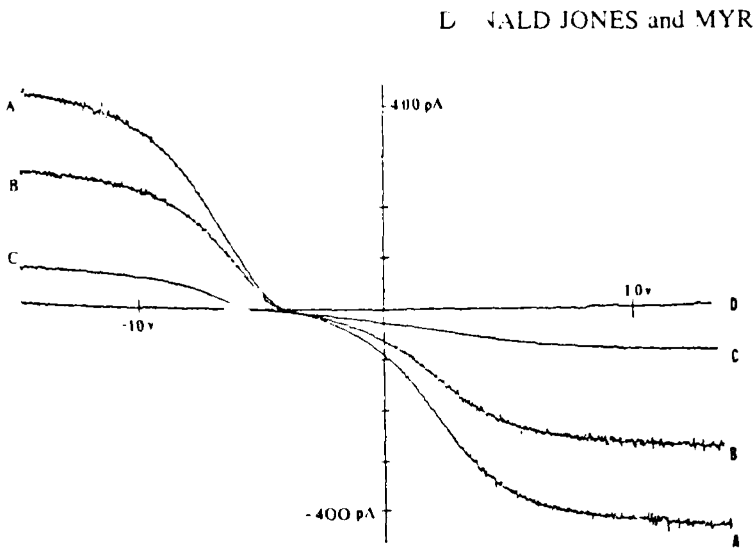

Fig. 2. Single-probe characteristics of stoichiometric CH_4–F_2 flames: (A) 2.5% O_2, (B) 1.5% O_2, (C) 0.4% O_2 (commercial fluorine), (D) purified fluorine (indistinguishable from baseline taken with no gas flows).

for O_2 impurity for CH emission in ClF_3-supported combustion. However, it is likely that there are considerable differences in the mechanisms of F_2 and ClF_3-supported combustion. For example, F_2 is a very weakly bound oxidant molecule, which is probably almost completely dissociated in the preheating zone of a premixed flame. The stronger bonds in ClF_3 allow it, as well as ClF_2 and ClF, to survive into the reaction zone of the flame. Since ClF_2 should be an effective free radical scavenger, much lower atom and free radical concentrations are anticipated in a ClF_3-supported flame than in the corresponding F_2 flame, which could explain the absence of CH emission from the ClF_3 system. The increase in $I(CH)/I(CHF)$ with increasing F_2 in our CH_4-rich premixed flames (and in those of Fedotov et al. [11]) could be due to increasing temperature as the flame approaches the stoichiometric ratio. Temperature increase could also account for the dramatic increase of $I(CH)/I(CHF)$ with pressure shown in Fig. 1 (and in the reports of Patel [3] and Fedotov [11]). While adiabatic temperatures rise only modestly over small pressure ranges [12], actual increases in temperature are much larger due to reduced heat and radical loss at higher pressure.

Since ionization is reduced to undetectable levels when O_2 impurity is removed from CH_4–F_2 flames, we conclude that ionization is not an intrinsic property of these flames. Thus, if F_2–hydrocarbon systems are employed for propulsion, it may be worthwhile to use purified fluorine in order to minimize interference of the exhaust with electromagnetic signals. Ionization is probably produced by reaction (2) in flames burning in commercial fluorine. The studies of infrared laser-excited mixtures of SF_6 with hydrocarbons [9] might appear to contradict our result. However, in the laser study ionization could have been produced either by the reactions of very highly vibrationally excited hydrocarbon radicals or by the reactions of sulfur-containing species, such as SF_5. In addition, it is not possible to rule out completely oxygen contamination in this work, since impurity levels are not discussed in the report.

Single-probe characteristics are usually very asymmetric, due to the predominant negative charge carriers (electrons) having much higher thermal velocity than the positive ions. However, in the presence of fluorine-containing additives nearly equal positive and negative saturation currents have been reported [13]. In the present work, rapid removal of thermal electrons is anticipated by the *exothermic* dissociative attachment reaction.

$$e + F_2 \rightarrow F + F^-, \tag{3}$$

and other electron attachment reactions. The "kinks" in the probe characteristics could result from two negative charge carriers with very different masses, i.e. electrons and negative ions.

A number of mechanisms involving only hydrocarbon species, i.e.,

$$CH^* + C_2H_2 \rightarrow C_3H_3^+ + e, \tag{4}$$

have been suggested as alternative mechanisms to (2) to explain ionization in hydrocarbon-oxygen combustion under particular conditions [14]. It is likely that there are copious quantities of hydrocarbon radicals and excited states in F_2–hydrocarbon flames. Thus, the present experiments, in which no ionization was detected in oxygen-free F_2–CH_4 and F_2–C_2H_2 flames, provide additional evidence that mechanisms not involving oxygen species are not likely to be important routes for producing ions in hydrocarbon–oxygen combustion.

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PERSISTENT LUMINESCENCE AS AN INDICATOR OF THE ENDPOINT OF CHEMILUMINESCENT TITRATIONS

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We have found that a powerful method of exploring bimolecular chemical reactions is to study their long time behavior. At the stoichiometric ratio of reactants, the decay of reagents in such systems is second order and thus inversely proportional to time. At any other concentration ratio of reactants, the reaction eventually becomes pseudo first order, with the limiting reagent decaying exponentially. Since exponential decay is much faster than 1/t decay, at the stoichiometric ratio reaction persists for a longer time than at any other ratio of concentrations. Thus the rate of reaction at long times varies by many orders of magnitude for small variations around the stoichiometric ratio of concentrations. Although the above results are interesting when applied to simple bimolecular reactions, we have by both analytical and numerical methods shown that similar results are obtained for more complicated mechanisms. Mechanisms consisting of reactions in series and in parallel are considered.

In order to make use of the above principle, it is necessary to be able to measure rates of reaction at fairly long times, where concentrations have decayed considerably from their initial values. One very sensitive method of quantifying reaction rates under such conditions is by observing chemiluminescence from reaction products. If the products decay quickly, chemiluminescent intensity is an instantaneous measurement of reaction rate.

Sharply peaked luminescence provides a general endpoint indicator for gas-phase titration reactions, which can be employed to measure the concentration of reactive species (such as atoms and free radicals) in kinetics studies. If the reactive species (whose concentration cannot be directly measured) undergoes a chemiluminescent reaction with a stable species (whose concentration can be measured), the observation of "persistent" chemiluminescence indicates the stoichiometric proportion of reactants. As one example of this general principle, the sharply peaked luminescence in the F + NO reaction is discussed. Since in this case, the titration is based on a combination reaction, fairly high pressures are needed to achieve a sufficient number of half lives of the reaction. The titration is thus complementary to another fluorine atom titration suggested a number of years ago.[1,2] That titration, with Cl_2, works best at low pressures. We believe that titration reactions for many other atoms and radicals will be developed based on this principle of "persistent luminescence".

Besides providing stoichiometric information, the shape of the titration curve gives information concerning the kinetics of the titration reaction. In order to reliably measure rate constants by this method, the kinetic analysis, based on the plug-flow approximation must be extended to include the effect of axial diffusion. The coupled second-order differential equations for a second-order reaction including flow and axial diffusion are solved numerically using a difference equation technique.

1. P. S. Ganguli and M. Kaufman, Chem. Phys. Lett. **25**, 22 (1974)
2. P. C. Nordine, J. Chem. Phys. **61**, 224 (1974)

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Kinetic Titrations

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Abstract: The equivalence point of the titration in a simple bimolecular reaction can be defined kinetically as the ratio of concentrations of reactants that results in maximum persistence of the reaction. This follows from the kinetics of the reaction remaining second-order at the stoichiometric ratio, whereas at any other ratio the reaction eventually becomes pseudo-first-order, with exponential decay of the limiting reagent. With allowance for axial diffusion, the shape of the titration curve can provide the rate constant of the titration reaction. The equivalence points for many titration reactions that proceed by mechanisms involving a series of reactions are predicted to be accurately indicated by the point of maximum persistence. However, some parallel reactions, such as wall or homogeneous loss of titrant or analyte, can distort the titration curve. Maximum persistence end points in agreement with theory are demonstrated for the O_3 + NO reaction, monitored by chemiluminescence in a low-pressure flow reactor.

A titration reaction

$$A + B \rightarrow \text{products} \qquad (1)$$

is a means of determining an amount of an analyte (A) by reacting it with an equivalent amount of titrant (B). Usually the titration reaction proceeds essentially to completion, so that its equivalence point can be identified as the amount of titrant (or the flow of titrant, if a steady flow of analyte is being determined) that must be added to the analyte so that neither titrant nor analyte remains. The assumption is usually made that the titration reaction is sufficiently rapid so that only the stoichiometry and not the kinetics of the titration reaction must be considered.

In the present work, an alternative approach to titration reactions, which explicitly focuses on their kinetics, is considered. In this approach the equivalence point of a titration reaction is identified as the ratio of titrant to analyte concentrations that results in "maximum persistence", i.e., maximum rate of the reaction at long times. At sufficiently long times, the reaction rate of a simple bimolecular reaction such as (1) is a very sharply peaked function of reactant ratio, allowing the equivalence point to be easily identified. This follows from a second-order reaction becoming pseudo-first-order if one of the reactants is present in great excess. As long as the reactants are not present in stoichiometric proportions, the limiting reagent will eventually be consumed to the point that its concentration will be much smaller than that of the other reagent. At times later than this, pseudo-first-order (exponential) decay of the limiting reagent will occur. Since at the stoichiometric ratio decay is second-order (proportional to $1/t$ at long times), the stoichiometric mixture will always decay more slowly than mixtures with any other proportion of reactants. Peaking of decay times at the stoichiometric ratio has also been reported in studies of relaxation kinetics.[1]

It will be shown that the titration curve can provide the rate constant of the titration reaction, as well as its equivalence point. Methods of experimentally observing the point of maximum persistence will be discussed, and the effect of diffusion on the results in flow systems will be considered. The results will be extended to titrations that proceed by a series of reactions, showing under what conditions a maximum persistence equivalence point is observed and exploring the shape of the titration curve for such reactions. Finally, parallel reactions will be considered, allowing the effect of first- and second-order loss of analyte to be evaluated. In the Experimental Section, agreement with theory is demonstrated for the NO + O_3 titration, monitored by chemiluminescence.

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(1) Winkler-Oswatitsch, R.; Eigen, M. *Angew. Chem., Int. Engl. Ed.* **1979**, *18*, 20.

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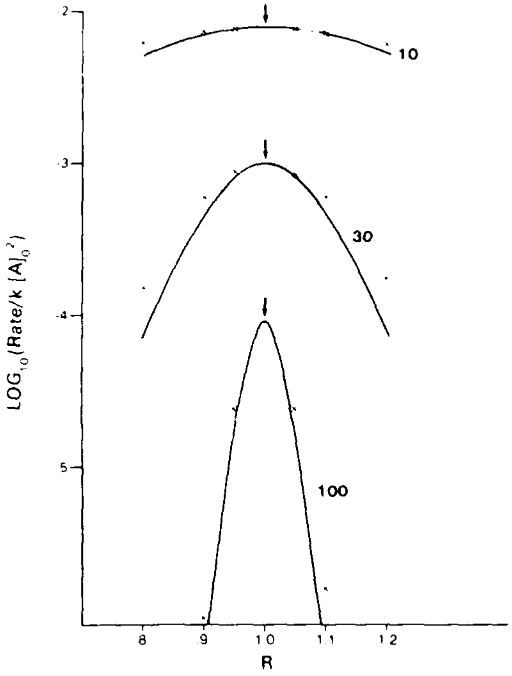

Figure 1. Curves: logarithm of the ratio of the reaction rate to the initial rate at the equivalence point as a function of the ratio of initial concentrations of reactants for a simple bimolecular titration reaction. Curves are given for $\vartheta = k[\mathrm{A}]_0t$ = 10, 30, and 100. Diffusion is not included in these calculations. Crosses: corresponding quantities for a two-step mechanism with $k_1 = k_2$.

Theory

Case I: Simple Bimolecular Reaction. The rate equation for a simple bimolecular mechanism can be solved by the method of partial fractions,[2] to give

$$\ln \{[\mathrm{A}]_0([\mathrm{B}]_0 - x)/([\mathrm{B}]_0([\mathrm{A}]_0 - x))\} = k([\mathrm{B}]_0 - [\mathrm{A}]_0)t \qquad (1)$$

The rate of the reaction can then be written as

$$\text{rate} = k[\mathrm{A}]_0^2R\left[1 - \frac{(e^{(1-R)\vartheta} - 1)}{(e^{(1-r)\vartheta} - R)}\right]\left[1 - \frac{R(e^{(1-R)\vartheta} - 1)}{(e^{(1-R)\vartheta} - R)}\right] \qquad (2)$$

where $R = [\mathrm{B}]_0/[\mathrm{A}]_0$ and $\vartheta = k[\mathrm{A}]_0t$.

The rate divided by $k[\mathrm{A}]_0^2$ is plotted as a function of R in Figure 1. The rate peaks very close to the stoichiometric ratio (within 0.4% at $\vartheta = 10$, much closer at larger ϑ). The peak is not very sharp at $\vartheta = 10$, but becomes increasingly sharp and reduced in intensity as ϑ increases. Considering the logarithmic nature of the plots, the end point of the titration would be easily located at values of $\vartheta \geq 30$. Since $\vartheta = k[\mathrm{A}]_0t$ is known from the shape of the titration curve, $[\mathrm{A}]_0$ from its end point, and t from distance and velocity in the flow system, k can be determined from the titration. At times shorter than those plotted in Figure 1, the maximum shifts progressively to higher values of R. (When very little A is consumed, intensity is proportional to the concentration of B.) For $R = 1$, expression 2 is undefined, but the rate can be found using L'Hopital's rule to be $k[\mathrm{A}]_0^2/(1 + \vartheta)^2$, which at long time becomes $1/kt^2$, i.e., independent of $[\mathrm{A}]_0$. Thus, at a given time (or position in a flow reactor), as the concentration of analyte decreases, the signal at the end point of the titration remains constant, but becomes more difficult to discern since the titration curve becomes broader.

In order to determine the equivalence point of a reaction by the method of maximum persistence, the reaction must be monitored by a technique that measures a property nearly proportional to the instantaneous rate of reaction. Light emission by the product of a chemiluminescent reaction is such a property, if the emitter is lost (by radiation and quenching) on a time scale that is rapid compared to the characteristic time of the reaction. In addition, the method by which reaction rate is monitored must have sufficient sensitivity for measuring this rate at long times, when the rate has declined by at least three orders of magnitude from its initial value (see Figure 1). The great sensitivity of photodetectors in the visible and ultraviolet region, together with the possibility of using these detectors in pulse-counting modes, will often satisfy this sensitivity requirement. In fact, in several cases ($\mathrm{F + H_2}$[3] and $\mathrm{F + CH_3OH}$[4]), we have *visually* identified maximum persistence end points. Other techniques that might be explored as end-point indicators for the method of maximum persistence are measurement of the fluorescence of a reactive intermediate or the heat generated by the reaction (assuming that the characteristic time for heat transfer can be made shorter than the reaction time). Kinetic titrations are cumbersome to perform in the time domain, requiring that the time course of the titration reaction be repeatedly followed with varying ratio of initial concentrations. Alternatively, in a continuous flow reactor, a fixed detector at a distance d samples the reaction mixture at time $t = d/v$, where v is the linear flow velocity in the reactor (assuming plug flow).

Effect of Diffusion. In real reactors operating in the laminar-flow regime, plug flow is modified by a parabolic dependence of velocity on radius (assuming a circular cross section) and by axial and radial diffusion. The equations for a second-order reaction then become:

$$v_0(1 - r^2/r_0^2)\frac{\partial[\mathrm{A}]}{\partial x} = D\left(\frac{\partial^2[\mathrm{A}]}{\partial x^2} + \frac{\partial^2[\mathrm{A}]}{\partial r^2} + \frac{1}{\mathrm{r}}\frac{\partial[\mathrm{A}]}{\partial r}\right) - k[\mathrm{A}][\mathrm{B}] \qquad (3)$$

$$v_0(1 - r^2/r_0^2)\frac{\partial[\mathrm{B}]}{\partial x} = D\left(\frac{\partial^2[\mathrm{B}]}{\partial x^2} + \frac{\partial^2[\mathrm{B}]}{\partial r^2} + \frac{1}{r}\frac{\partial[\mathrm{B}]}{\partial r}\right) - k[\mathrm{A}][\mathrm{B}] \qquad (4)$$

where v_0 is the flow velocity at the center of the reactor of radius r_0. It is assumed that A and B have the same diffusion coefficient, D. Because we are considering distances along the length of the flow tube that are many times its diameter, it will be assumed that all radial concentration gradients are eliminated by diffusion. Replacing the parabolic velocity distribution by its area-average value, $v = v_0/2$, then gives

$$-v\frac{d[\mathrm{A}]}{\mathrm{d}x} + D\frac{\mathrm{d}^2[\mathrm{A}]}{d^2\mathrm{x}} = k[\mathrm{A}][\mathrm{B}] = -v\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}x} + D\frac{\mathrm{d}^2[\mathrm{B}]}{\mathrm{d}x^2} \qquad (5)$$

or with $a = [\mathrm{A}]/[\mathrm{A}]_0$, $b = [\mathrm{B}]/[\mathrm{B}]_0$, $q = vx/D$, and $s = [\mathrm{A}]_0kD/v^2$ (s is a measure of the ratio of diffusive loss to reactive loss of the limiting reagent in the first-order regime.)

$$\frac{\mathrm{d}a}{\mathrm{d}q} = \frac{\mathrm{d}^2a}{\mathrm{d}q^2} - Rsab \qquad (6)$$

$$\frac{\mathrm{d}b}{\mathrm{d}q} = \frac{\mathrm{d}^2b}{\mathrm{d}q^2} - sab \qquad (7)$$

Equations 6 and 7 were converted to a set of four first-order differential equations and solved numerically by a difference equation method using IMSL program DVCPR.[5] The boundary conditions are $a = b = 1$ at $q_1 = 0$, and at a large value of q_2 (arbitrarily set to at least twice the largest value of interest), the

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(2) See, for example: Skinner, G. B. *Introduction to Chemical Kinetics*; Academic Press: New York, 1974; p 19.

(3) Ganguli, P. S.; Hertzler, B. L.; Kaufman, M. *Chem. Phys. Lett.* **1976**, *37*, 319.

(4) Bogan, D. J.; Kaufman, M.; Sanders, W. A.; Hand, C. W.; Wang, H.-t. Proceedings of Eastern Section of Combustion Institute, Dec 1982.

(5) IMSL Inc., 2500 City West Blvd., Houston, TX 77042-3020.

Table I. $-\log(\mathrm{Rate}/\mathrm{Rate}_{ls})$ for a Bimolecular Reaction with Axial Diffusion

$\mathcal{J}$	R: 0.8	0.9	0.95	1	1.05	1.1	1.2
				$s = 0$			
10	2.26	2.13	2.10	2.08	2.09	2.12	2.24
30	4.10	3.31	3.07	2.98	3.07	3.30	4.08
60	6.70	4.65	3.88	3.57	3.88	4.64	6.69
100	10.03	6.39	4.79	4.01	4.79	6.38	10.03
				$s = 0.2$			
10	2.17	2.06	2.03	2.02	2.02	2.05	2.15
30	3.96	3.24	3.03	2.95	3.02	3.24	3.94
60	6.47	4.57	3.85	3.55	3.84	4.56	6.45
100	9.82	6.27	4.75	3.99	4.74	6.27	9.80
				$s = 0.5$			
10	2.06	1.97	1.95	1.94	1.94	1.96	2.03
30	3.78	3.16	2.98	2.91	2.97	3.16	3.76
60	6.20	4.46	3.80	3.52	3.79	4.45	6.16
100	9.49	6.12	4.69	3.97	4.68	6.11	9.42
				$s = 1.0$			
10	1.95	1.87	1.85	1.84	1.84	1.86	1.90
30	3.58	3.06	2.90	2.84	2.90	3.06	3.55
60	5.82	4.32	3.73	3.48	3.73	4.31	5.79
100	8.78	5.91	4.61	3.95	4.60	5.91	8.75
				$s = 2.0$			
10	1.77	1.72	1.70	1.69	1.69	1.70	1.72
30	3.30	2.91	2.78	2.74	2.78	2.90	3.26
60	5.30	4.10	3.61	3.41	3.61	4.08	5.26
100	7.94	5.58	4.47	3.90	4.47	5.58	7.91
				$s = 5.0$			
10	1.50	1.47	1.46	1.45	1.44	1.44	1.44
30	2.84	2.62	2.55	2.53	2.55	2.60	2.80
60	4.47	3.69	3.38	3.25	3.38	3.68	4.44
100	6.62	4.98	4.18	3.78	4.18	4.96	6.58

limiting reagent concentration is set equal to zero and the other reagent to its excess. The results of the calculations for $\mathcal{J} = sq$ of interest, given in Table I, are found to be independent of considerable variation in q_2. With known D, k is determined by finding the value of s that best fits the shape of the titration curve at the experimental value of $x = D\mathcal{J}/sv$. In order to permit such fitting, an extensive table of rates as a function of $\mathcal{J}$ and s is given in the Supplementary Material.

The effect of including increasing amounts of diffusion in the calculation is to increase the reaction rate at any downstream point in the reactor as reagents diffuse from upstream. However, the effect of diffusion is relatively greater for ratios further from stoichiometric, since in these cases the limiting reagent concentration falls off much faster and thus provides a larger concentration gradient for diffusion. As a result, diffusion broadens the titration curves. Diffusion has very little effect on the end points of titrations, except at very low values of $\mathcal{J}$ and large amounts of diffusion, where the titration curve is almost flat.

Case II: **Two-Step Series Mechanism.** Persistent luminescence may also be observed in reactions that proceed by a multistep mechanism. Analysis of such systems may provide stoichiometric, mechanistic, and kinetic information. For example, consider the simple two-step series mechanism,

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{Y}$$

$$\mathrm{B} + \mathrm{Y} \xrightarrow{k_2} \mathrm{E}$$

where E is an emitting product. When $k_1 \ll k_2$, the steady-state approximation for Y, $[\mathrm{Y}] = k_1[\mathrm{A}]/k_2$, holds, giving the kinetic equation

$$\mathrm{d}x/\mathrm{d}t = k_1([\mathrm{B}]_0 - x)(2[\mathrm{A}]_0 - x) \qquad (8)$$

where x is the concentration of B consumed. With the substitution of $2[\mathrm{A}]_0$ for $[\mathrm{A}]_0$, this is clearly the same equation as holds for the simple bimolecular mechanism (I). Thus, if for this two-step series mechanism at steady state, emission intensity is plotted against R', where $R' = [\mathrm{B}]_0/2[\mathrm{A}]_0$, for $\mathcal{J}' = 2k_1[\mathrm{A}]_0t$, the curves would be identical with those shown in Figure 1.

In order to test the importance of the steady-state assumption for sharply peaked emission at the end point, the two-step series mechanism for $k_1 = k_2$, which clearly does not satisfy the steady-state condition, has been modeled using the Gear algorithm.[6] Results of this calculation are shown as crosses adjacent to the $\mathcal{J} = 30$ curve in Figure 1. Although there are small quantitative differences from the steady-state curves, the qualitative conclusion, that light emission at long times is sharply peaked at the stoichiometric concentration ratio, is still valid.

For the two-step mechanism, it is also possible to consider the limit $k_1 \gg k_2$. In this case, the first reaction goes rapidly to completion, consuming $[\mathrm{A}]_0$ of B. Luminescence from the second reaction then peaks at its equivalence point, when a second $[\mathrm{A}]_0$ of B is consumed. Light emission at long times is again strongly peaked at the equivalence point of the overall reaction ($[\mathrm{B}]_0 = 2[\mathrm{A}]_0$). However, the variation of luminescence around the equivalence point is now determined by the value of $\mathcal{J}' = k_2[\mathrm{A}]_0t$, since reaction 2 is rate limiting, and $[\mathrm{A}]_0$ of Y must react at the equivalence point of this reaction. In this case, $R' = ([\mathrm{B}]_0 - [\mathrm{A}]_0)/[\mathrm{A}]_0$, and no light is emitted in the first half of the titration. Such differences in the shape of the titration curve may allow mechanisms to be distinguished by studying persistent luminescence. Although we have not attempted a general proof, it appears that in the two-step series mechanism, long-time light emission will always peak very close to the equivalence point of the reaction.

Case III: **General Series Mechanism.** It is also possible to draw some conclusions regarding a general n-step series mechanism, of the form

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{Y}_1$$

$$\mathrm{B} + \mathrm{Y}_1 \xrightarrow{k_2} \mathrm{Y}_2$$

$$\mathrm{B} + \mathrm{Y}_2 \xrightarrow{k_3} \mathrm{Y}_3 \text{ etc.}$$

Only the case in which one reaction in the series is much slower than all the others will be discussed. If the first reaction in this mechanism is rate limiting, n B's will be consumed simultaneously for each A that reacts. Thus if the variables $R' = [\mathrm{B}]_0/n[\mathrm{A}]_0$ and $\mathcal{J}' = nk_1[\mathrm{A}]_0t$ are employed, this mechanism gives curves identical with those shown in Figure 1, regardless of which intermediate emits light.

If the initial reaction is not rate limiting, the results depend upon whether the rate-limiting reaction in the series comes before or after the production of the luminescent species. If the rate-limiting step comes before the production of the luminescent product, say after n' steps, $n'[\mathrm{A}]_0$ B's will be rapidly consumed with no luminescence, and all the initial A will be rapidly converted to $\mathrm{Y}_{n'}$. As more B is added, subsequent Y's will be in steady state with $\mathrm{Y}_{n'}$ and will all be formed at maximum long-term rates when just an additional $(n - n')[\mathrm{A}]_0$ of B is available. Once again maximum long-term emission will occur at the overall equivalence point, $[\mathrm{B}]_0 = n[\mathrm{A}]_0$. The variation of the emission around the end point will now be determined by the value of $\mathcal{J}' = (n - n')k_{n'+1}[\mathrm{A}]_0t$ and is in the variable $R' = ([\mathrm{B}]_0 - n'[\mathrm{A}]_0)/((n - n')[\mathrm{A}]_0)$. If, however, the rate-limiting step occurs after the formation of the luminescent intermediate, the buildup of the slowly reacting intermediate will result in pseudo-first-order decay of B, and no persistent luminescence will be observed. It is suggested by these considerations and the modeling for $k_1 = k_2$ in the two-step mechanism that, if persistent luminescence is observed in a series of reactions, maximum persistence should occur at the equivalence point of the overall reaction.

Case IV: **Parallel Mechanisms.** One important parallel mechanism is

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[6] Gear, C. W. *Numerical Initial Value Problems in Ordinary Differential Equations*; Prentice-Hall: Englewood Cliffs, NJ, 1971.

$$A + B \xrightarrow{k_1} E$$

$$A \xrightarrow{k_2} P$$

This mechanism holds when either analyte or titrant are consumed by a wall reaction. Noting that

$$d[A]/d[B] = (k_1[B] + k_2)/k_1[B] \tag{9}$$

we obtain

$$[A] = [A]_0 + ([B] - [B]_0) + (k_2/k_1) \ln ([B]/[B]_0) \tag{10}$$

which when substituted into $d[B]/dt = -k_1[A][B]$, with $R = [B]_0/[A]_0$, $b = [B]/[B]_0$, and $h = k_2/(k_1[B]_0)$, gives

$$k_1[B]_0 t = \int_b^1 db'/(b'(1/R + (b'-1) + h \ln b')) \tag{11}$$

This equation has been numerically integrated using Simpson's rule, showing that if $h < 10^{-3}$, the results are indistinguishable from the curves in Figure 1. However, for $h = 10^{-2}$ the differences from Figure 1 are substantial. For titrations involving stable molecular analytes and titrants, these considerations will generally not be important. For atoms and radicals, undistorted titration curves will usually be achieved in cases in which the titration reactions are fast and the walls can be treated to avoid loss of the analyte.

Another parallel mechanism of interest involves two competing second-order reactions:

$$A + B \xrightarrow{k_1} E$$

$$A + A \xrightarrow{k_2} P$$

This mechanism would hold, for example, if an analyte undergoes homogeneous recombination simultaneously with being titrated. In this case, if

$$[B]/[A] = 1 - k_2/k_1 \tag{12}$$

then

$$d[A]/d[B] = (k_1[B] + k_2[A])/(k_1[B]) = [A]/[B] \tag{13}$$

and the ratio of A to B will not change, resulting in second-order kinetics and maximum persistence. Thus, the end point of this titration will be displaced by an amount k_2/k_1 from the equivalence point of the first reaction. The titration curve will be asymmetric, since with excess [A], A will decay relatively faster than B until (12) is reached, after which decay will be by second-order kinetics. However, with any excess B, the reaction will tend toward pseudo-first-order decay.

The final mechanism considered is

$$A + B \xrightarrow{k_1} E$$

$$B + C \xrightarrow{k_2} P$$

This mechanism is important, for example, if there is an impurity in the system that reacts with the titrant. If in this mechanism, $k_2 < k_1$, C will persist at long times and eventually the decay of B will become pseudo-first-order. Thus, simultaneous decay of A and B will not be possible. Of course, whether persistent decay of luminescence is perceived or not will depend on the relative rates of the two reactions and the relative concentrations of A and C. A very small concentration of a very slowly reacting "impurity" will clearly have little effect on the titration.

If $k_2 > k_1$, reaction with C will be essentially complete before the end point is reached, and maximum persistence will be achieved when $[B]_0 = [A]_0 + [C]_0$. In this case the variation of intensity around the end point will be determined by the value of $\mathcal{J} = k_1[A]_0 t$ and be in the variable $R' = ([B]_0 - [C]_0)/[A]_0$.

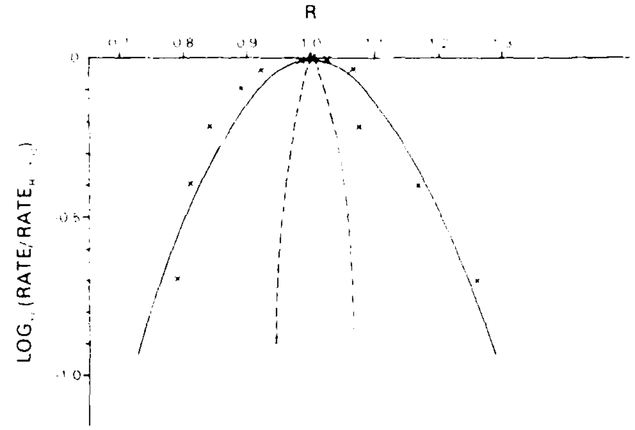

Figure 2. Points: logarithim of the ratio of the measured chemiluminescence of the NO + O_3 reaction to the peak value of chemiluminescence as the ratio of NO to O_3 (R) is varied. Curves, theory for comparison with experiment: (—) at $\mathcal{J} = 21.3$, $s = 0.36$; (- - -) at $\mathcal{J} = 99.6$, $s = 2.2$.

Comparison with Experiment. The chemiluminescent reaction of O_3 with NO was chosen for comparison with theory since it is known to produce emitting NO_2 by the simple mechanism:[7]

$$O_3 + NO \xrightarrow{k_{II}} NO_2 + O_2 \tag{II}$$

$$O_3 + NO \xrightarrow{k_{III}} NO_2^* + O_2 \tag{III}$$

$$NO_2^* \xrightarrow{k_r} \text{light} \tag{IV}$$

$$NO_2^* + M \xrightarrow{k_q} NO_2 + M \tag{V}$$

Reactions II and V do not complicate the analysis, but do reduce the intensity of the photosignal, as does the poor overlap of the sensitivity of the phototube with the spectral distribution of the chemiluminescence, which peaks at ca. 1300 nm.[8] The overall rate constant, $k_{II} + k_{III}$, reported to be $2.0 \pm 0.2 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1},[9] is used in the case I analysis. Besides its simple mechanism, added advantages of the O_3 + NO reaction as a prototype are that wall reactions are probably negligible and that the diffusion coefficients of the reagents do not differ greatly.

Titrations of O_3, at concentrations of 3.6×10^{14} and 1.8×10^{15} cm^{-3} in O_2, are shown in the logarithimic curves of Figure 2. For the diffusion coefficient (which should be the average of values for O_3 and NO in O_2), a value of 33 cm^2 s^{-1} at 4.3 Torr is employed.[10] The two runs correspond to $\mathcal{J} = 21.3$, $s = 0.36$ and $\mathcal{J} = 99.6$, $s = 2.2$, respectively. As predicted by the case I theory, the peak intensity of the titration curve is found to vary less than 10% with initial concentrations of ozone varying by more than a factor of 4.

Notwithstanding the considerable scatter of the experimental points, due to the weak photosignal and the difficulty in measuring the very small variations in flow of the NO titrant, the agreement between theory and experiment is quite satisfactory. Thus the theory seems adequate for the present experiments. A simple change in the theory, which might be appropriate for more precise data or for experiments involving reactants of very different size, would be to use different diffusion constants on each side of the equivalence point. (The constant for the limiting reagent in each regime should be employed.)

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(7) Clyne, M. A. A.; Thrush, B. A.; Wayne, R. P. *Trans. Faraday Soc.* **1964**, *60*, 359.

(8) Kenner, R. D.; Ogryzlo, E. A. In *Chemi- and Bioluminescence* Bur, J. G., Ed.; M Dekker, New York, 1985; p 137.

(9) Michael, J. V.; Allen, J. E., Jr.; Brobst, W. D. *J. Phys. Chem.* **1981**, *85*, 4109.

(10) For O_3 in O_2: Houzelot, J. L.; Villemaux, J. *J. Chim. Phys. Phys.-Chim. Biol.* **1977**, *74*, 229. For NO in O_2, an experimental value for CO in O_2 is used from: Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954; p 579.

Another system in which persistent luminescence has been observed is F_2 + NO, where light, presumably from FNO[11] peaks at $[NO]_0 = 2[F_2]_0$. As previously mentioned, sharply peaked downstream emission has also been observed in the F + H_2[3] and F + CH_3OH[4] reactions. These systems are all more complicated than O_3 + NO, containing possibilities of series and parallel reactions. Their detailed analysis has not yet been completed.

Experimental Section

Chemiluminescence from the NO + O_3 reaction was studied in a 2-in. diameter Teflon-coated Pyrex flow tube at 25 °C and 4.3 Torr with luminescence observed ca. 70 cm downstream of the mixing zone by a cooled R406 photomultiplier. The flow velocity was 25 cm/s. A steady flow of ozone was obtained in O_2 diluent by directing the output from a Wellsbach Model T406 ozonizer directly into the flow tube. At full voltage the ozonizer produces ca. 2% ozone, at which concentration the titration is too sharply peaked to give a meaningful comparison with theory. However, when the voltage of the ozonizer is reduced to 60-75 V, it produces ca. 0.25-1.25% O_3 (as measured by the end point of the titration) and gives the titration curves shown in Figure 2. Nitric oxide (Linde) was taken directly from a lecture bottle. Its flow was adjusted by means of a Granville-Phillips metal seal series 203 variable leak. The flow from the ozonizer was measured by a Brooks mercury piston flowmeter and that of NO by directing the flow into an evacuated calibrated volume and measuring the rate of pressure increase in the volume. System pressure was measured with a 0-100 Torr MKS Baratron gauge. Flows were permitted to stabilize for several hours before taking measurements.

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Supplementary Material Available: Table of rates as a function of d and s (5 pages). Ordering information is given on any current masthead page.

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[11] Johnston, H. S.; Bertin, H. J., Jr. *J. Mol. Spectrosc.* **1959**, *3*, 683.

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Mechanisms producing luminescence from CH, C_2 and CHF in CH_4-F_2 flames are investigated by the method of very dilute flames, where small additions of CH_4 are made to H_2-F_2 flames. By this technique, the dependence of the emission intensities are systematically studied as a function of the concentrations of carbon radicals and H and F atoms in the flame. C_2 emission is found to be due to the reaction of two CH radicals, while CH emission (both A and B states) and CHF emission results from vibration-to-electronic energy transfer from vibrationally excited HF. Experiments using CD_4 confirm the mechanisms for the CH emission. Because fluorine is a monovalent oxidizer, the chemistry of fluorine flames is simpler than that of the analogous oxygen system, and mechanisms for luminescences can be more easily established in the fluorine flames.

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Luminescence from Dilute Methane-Fluorine Flames

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Introduction

Besides the inherent interest of fluorine-supported combustion for lasers and advanced propulsion systems, such flames are also important for what they can reveal about combustion processes in general. Luminescence from CH and C_2 have been shown to be a common property of fluorine[1] and oxygen-supported[2] combustion of hydrocarbons. In the oxygen flames, decades of experimentation have not succeeded in establishing <u>all</u> the mechanisms producing these luminescences. If mechanisms for these emissions could be determined in fluorine flames, and if these mechanisms did not explicitly involve fluorine-containing species, the same mechanism might make a substantial contribution in oxygen flames.

Notwithstanding their higher temperatures and burning velocity, fluorine flames are intrinsically simpler than oxygen flames. This is a result of fluorine being monovalent rather than divalent. There are no species analogous to peroxides and aldehydes to complicate fluorine-based combustion. Thus, mechanisms for light emissions can be more easily established in fluorine than in oxygen-supported combustion. In addition, there are no multiple bonds to fluorine, forming compounds with bond strengths comparable to CO. Thus, if an emitting state is to be populated in a single reaction, there are usually fewer energetically feasible routes for producing the state in a fluorine flame than in the corresponding oxygen flame.

A very powerful method for studying mechanisms of luminescences in hydrocarbon flames is the method of very dilute flames. As applied to oxygen-supported combustion by van Tigglen and others[3], very small amounts of hydrocarbons are added to H_2-O_2 flames. Trace additions of hydrocarbons at these levels do not appreciably change the basic flame parameters, such as flame temperature, burning velocity and the concentration of H, O and OH radicals. Thus, the dependence of various luminescences exclusively on the concentration of hydrocarbon and carbon-containing radicals can be probed. Alternatively, the known variation of the properties of the H_2-O_2 flame as its equivalence ratio is varied can be used to probe the dependence of the luminescence on the concentration of H, O and OH radicals.

In addition to luminescence from CH and C_2 radicals, low pressure F_2-hydrocarbon flames also show emission from

CHF radicals and highly vibrationally excited HF molecules. In the ultraviolet, emission from CF and CF_2 is observed. Under some conditions luminescence from C_3, soot particles and impurity-derived OH is also detected. The various emissions show surprisingly large variation in relative intensity as flame conditions are varied. In the present work, we systematically study the variation of the intensities of the CH, C_2 and CHF emissions as conditions are varied in H_2-F_2 flames containing very low concentrations of methane, with the aim of establishing the mechanisms for the emissions in fluorine combustion, and perhaps contributing to their understanding in other forms of combustion as well.

Experimental

Premixed H_2-F_2 flames were burned on a 1/8-inch id water-cooled burner in a previously-described[1] vacuum chamber. Calibrated Union Carbide mass flow sensors were used to monitor flows, and fuel flows were controlled with flow controllers. Prssure in the vacuum chamber was regulated with a valve in the exhaust line. Luminescence was monitored through a calcium fluoride window by a 0.25-meter Jarrell-Ash monochrometer with either a R446 photomultiplier (200-800nm) or a cooled R406 photomultiplier (880-950nm). The response of the system with the latter tube was calibrated against a 1275K blackbody. Low concentrations of CH_4 were added to the flames by replacing part of the H_2 flow with an equal flow of a 1.91% CH_4 in H_2 mixture prepared by Matheson. When studying flames of CD_4 (Cambridge Isotope Laboratories), this fuel was added neat to H_2-F_2 flames.

Systematic studies were made of the dependence on equivalence ratio and pressure of the intensity of the $A^2\Delta \rightarrow X^2\Pi$ and $B^2\Sigma^- \rightarrow X^2\Pi$ transitions of CH, the $A\ ^1A'' \rightarrow X^1A'$ transition of CHF and the $A^3\Pi_g$--$X^3\Pi_u$ (Swan bands) of C_2. The (0,0) band of the $A^2\Sigma^+ \rightarrow X^2\Pi$ transition of OH was often monitored as a measure of the oxygen impurity in the system. The following vibrational-rotational bands of HF were observed: (5-0), (6-1), (7-2), (8-3) and (9-4) of the $\Delta v = 5$ sequence; (4-0), (5-1), (6-2), (7-3), (8-4) and (9-5) of the $\Delta v = 4$ sequence and (3-0) and (4-1) of the $\Delta v = 3$ sequence. The rotational temperatures of the HF (3-0) band was measured using intensities determined by the calibrated photomultiplier and F factors reported in the literature.[4,5]

Results

The visual appearence of dilute CH_4-F_2 flames at pressures typical of our experiments (6 Torr) varied with equivalence ratio of the flame. For lean flames (ER =

0.5-0.8), the flames were roughly hemispheres of ca. 1/4-inch radius. Most of the visual flame was yellowish-white, except for a thin band at the top of the flame that was blue. The emitting region of these flames had a distinct boundary, beyond which no emission could be visually detected. Rich flames (ER = 1.2-1.5) at the same pressure were bluish-green in color and much dimmer than the lean flames. The outer boundary of the rich flames was not distinct; it trailed off into a blue region of slowly diminishing intensity that was visible for at least one inch from the burner. Without added CH_4, the flames were hardly visible, emitting only extremely weak red radiation. When photographed with infrared sensitive film, the infrared emitting region was seen to be about the size of the visible lean flame. The infrared emitting region changed only slightly in size as ER was varied, being a little larger for the stoichiometric mixture than for either lean or rich flames.

Measured HF (3-0) rotational temperatures for H_2-F_2 flames at 7.7 Torr total pressure are given as a function of ER in figure 1. T_r is fairly constant at 2000±150 K for lean flames, but falls off fairly rapidly for rich flames. Also given in figure 1 are the calculated adiabatic flame temperatures at 7.7 Torr. These are much higher than the measured T_rs and show much less variation with ER. Measured

T_r increases from ca. 1500K to ca. 2000K as pressure is increased from 3 to 10 Torr. In addition T_r increased by about 200K when 1% CH_4 was added to the flame.

The dependence of the intensity of CH (A state) emission at 430nm, of CHF emission at 518 nm and C_2 emission at 516 nm, as a function of the amount of CH_4 added to a 7.1 Torr H_2-F_2 flame is given in figure 2. CHF intensity varies linearly, CH intensity close to linearly and C_2 as the square of the added CH_4. The intensities of these emissions as a function of ER (at 10.2 Torr) is shown in figure 3. CHF emission is fairly constant for lean flames and falls off slowly as ER is increased to 1.5. By contrast CH and C_2 emission peak at ER of ca. 0.8 and then fall off rapidly for rich flames. As shown in figure 4, as pressure is increased from 4 to 12 Torr, CH emission (both A and B states) increases by a factor of 7 and C_2 emission by a factor of 25, while CHF emission decreases by half. The intensity of CH emission increases much faster with pressure in lean flames than in rich flame. The ratio of CH A state to B state emission intensities remains remarkably constant (to 1%) as pressure is varied over this range. In experiments in which 2% CD_4 was added to a H_2-F_2 flame, emission in both the A→X and B→X transitions were found to have at least 50% of their intensity due to CD.

Discussion

In discussing mechanisms for CH, C_2 and CHF luminescence in dilute CH_4-F_2 flames, we will employ a simplified description of these systems rather than a comprehensive consideration of reactions regardless of their importance in these flames. Variations of the emissions with respect to changes in added CH_4 and in equivalence ratio and pressure will first be discussed in terms of the most important properties of the dilute flames.

The burning velocity and adiabatic flame temperature of H_2-F_2 flames are among the highest known in combustion. For example, at 7.7 Torr total pressure, the adiabatic flame temperature of H_2-F_2 flames varies over the range 3260K to 3120K as the equivalence ratio varies from 0.5 to 1.5. T_{ad} peaks at 3260K for an equivalence ratio of 0.85. The reason for higher adiabatic temperatures for lean flames is that all F_2 and almost all H_2 is dissociated at equilibrium in these flames, and dissociation of H_2 consumes more energy. T_{ad} increases with pressure, since it is largely determined by the fractional dissociation of HF, which decreases as the pressure increases.

The measured rotational temperatures of the HF 3→0 vibration-rotation band peaks for slightly lean flames at a value over 1000K below T_{ad}. In rich flames the measured T_{rot}

falls off much faster than does the calculated adiabatic flame temperatures. The photographs of the infrared emitting region of the flame show that this region is largely concentrated very close to the burner. This region must have a much greater concentration of HF states with $v > 3$, emission from which the film is sensitive, than the outer regions of the flame. Thus, the emitting region manifests much of the hot nascent vibrational distribution of the H_2-F_2 chain reaction. Since the emitting region has excess vibrational energy, its rotational and translational energies must be lower than the adiabatic temperature. It is therefore not surprising that T_r measurements in the (3-0) band of HF, which probably sample the same region as the infrared images, yield values considerably lower than the adiabatic flame temperature. The observation that deviations from T_{ad} are greater in rich flames may be due to vibrational energy of HF being efficiently transferred to vibrational and rotational energy of H_2 in such systems. The infrared photos indicate that the H_2-F_2 chain reactions

1) $F + H_2 \longrightarrow HF + H \quad \Delta H = -31.9$ kcal/mole, and

2) $H + F_2 \longrightarrow HF + F \quad \Delta H = -98.4$ kcal/mole

are largely complete very close to the burner. Beyond this region, the flame "bath" consists of HF molecules, whose vibrational distribution is rapidly relaxing, free atoms, with a preponderance of the atom present in excess, and, in the case of rich flames, excess H_2 (F_2 would be almost completely dissociated).

Methane and CH_x radicals react with F atoms at speeds comparable to that of reaction (1). Thus in lean flames, the reactions of the carbon-containing radicals occur practically simultaneous with reactions (1) and (2), and the region of the flame emitting the CH, C_2 and CHF band is also located very close to the burner. In rich flames, however, where the ratio of F atoms to H atoms is small, the rate-limiting step for CH_4 consumption is the reaction

(3) $H + CH_3 \longrightarrow H_2 + CH_2 \quad \Delta H = 5.2$ kcal/mole,

which must have an activation energy at least equal to its endothermicity. There is no experimental determination of the rate constant of this reaction. In fact, at typical flame conditions, reaction (3) is usually considered to be slow compared with the competing reaction[6]

3') $H + CH_3 + M \longrightarrow CH_4 + M$.

One study completely neglects (3) in comparison to (3′) at 753K and 8 Torr.[7]. Since reaction (3′) returns carbon to unreacted methane, we can anticipate a bottleneck in removing the second hydrogen from methane in rich flames. As a result of this, radicals smaller than CH_3 are formed only slowly and reach their maximum concentration in the outer regions of the flame. In addition, since the rate of destruction of CH_2[8] and CH[9] with H atoms are fast, the concentrations of such radicals do not build up to very high levels in rich flames. The dominance of reaction (3) in determining luminescence variations is illustrated by the spacial variation of the visible luminescences from the dilute flames. For lean flames, the visible light comes almost exculsively from a very small region near the mouth of the burner (comparable to the infrared emitting region), while in rich flames the visible region is many times larger.

Acceptable mechanisms for CH, C_2 and CHF emission not only have to be in accord with this simple picture of the dilute CH_4-F_2 flame, but also have to involve reactions for producing the emitting states that are exothermic or only mildly endothermic. Hopefully, in considering energetically feasible reactions, only one or a few will be in accord with the variation predicted by our simple model of the dilute flame. In addition, since it is always possible to rationalize the parametric dependence of an emission intensity by invoking a large number of different mechanisms, we will be particularly encouraged if a single mechanism can explain the observed variation.

<u>CH emission</u>

In order to excite the A state of CH, 66.3 kcal/mole is required (82.1 kcal/mole for the v = 2 level, which is observed in lean flames). For the B state of CH, 74.4 kcal/mole is needed. We have not noted emission from the C state, but very weak C-state emission may be obscured by OH bands (resulting from oxygen impurity in the fluorine). Since we have previously noted that the intensity of CH emission is undiminished when oxygen is removed from the system[1], these emissions must be explained without recourse to reactions involving formation of strong C-O bonds. We have been able to identify only two reasonable reactions with sufficient exothermicity to excite the observed emitting states in CH. These are: atomic combination

4) $C + H + M \longrightarrow CH + M$ $\Delta H = -81$ kcal/mole, and

energy transfer to CH from vibrationally excited HF.

5) $CH + HF^{*} \longrightarrow CH + HF$,

which would require transfer from v = 9 in HF (for v = 2 of the A state), if the energy is supplied in a single step. More likely, would be a multistep transfer through vibrationally excited CH(X), facilitated by the similarity in the vibrational constants of HF and CH.

An acceptable mechanism must be able to explain the observations that CH emission intensity peaks in lean flames, is close to linearly dependent on the CH_4 added to the flame, and rises dramatically with pressure. In addition, in lean flames the blue emitting region at the top of the flame abruptly terminates at about the end of the strongly infrared emitting region. Reaction (4) is completely unable to explain the observations in lean flames. If appreciable concentrations of F_2 remain thermally undissociated at the top of the bright lean flame, such concentrations of F_2 would reduce C and H to negligible concentrations. If no F_2 survived into this region, there would be no reason for the sudden termination of the emitting region, since H and C atoms would decay very slowly in the absence of F_2. Additionally, in lean flames, where CH_4 is broken down rather quickly, a considerable fraction of the total carbon would be tied up as strongly bonded fluorine-containing species, due to reactions such as:

6) $CH_3 + F_2 \longrightarrow CH_3F + F$, and

7) $F + CH_3 \longrightarrow CH_2F + H$,

and intense emission would not be anticipated. These arguments rule out atom combination as an important route for generating CH emission in our dilute flames. The experiments using CD_4 definitely confirm this conclusion. In the flame resulting from 2% CD_4 added to a lean H_2-F_2 mixture, almost all free hydrogen atoms are the H isotope.

(Most D atoms are stripped by F atoms to become unreactive DF.) Reaction (4) would thus predict almost exclusive CH A and B state emission, in constrast to what is observed. .

Reaction (5), however, provides a very good explanation for the intensity variation of CH emission. Here the determining factor is the overlap of the region of appreciable CH concentration and the region of vibrationally hot HF molecules (ie, the infrared emitting region). As equivalence ratio is increased, stripping of H from methyl radicals becomes dominated by the slow reaction (3), thus effectively separating CH radicals from vibrationally hot HF molecules. Reaction (5) predicts a linear increase in CH intensity with added CH_4, which is close to what is observed. This mechanism also predicts the predominance of CD emission in the flames with CD_4. Scrambling reactions, such as

8) $CD + H_2 \longrightarrow CDH + H$, and

9) $H + CD \longrightarrow CH + D$,

could explain the CH emission that is observed in the CD_4 experiments.

The primary result of increasing pressure is to compress the flame. As a result, if mole fractions remain the same, the integrated intensity resulting from a second-order chemiluminescent reaction should increase approximately linearly with pressure. Additionally, as pressure is increased, flame temperature rises (due to an increase in the adiabatic flame temperature and a decrease in heat loss from the reaction region). At higher temperatures thermal dissociation of F_2 is more rapid, producing a general increase in the mole fraction of all radical species. In lean flames the rate of increase of the intensity of A state and B state CH emission are remarkably similar and roughly proportional to $P^{1.85}$. This rise is in accord with what is anticipated due to compression and temperature increase. In rich flames, however, the rate of increase of CH emission with pressure in the range 4-10 Torr is less than linear. In this case the overlap between vibrationally excited HF molecules and CH radicals may decrease due to increased vibrational relaxation of HF by H_2 at higher pressures. The near constancy of the ratio I_B/I_A under conditions which surely must change the vibrational distribution of HF molecules, strongly suggests that branching into the A and B states at constant ratio occurs from a common level after the CH radicals have received energy from the HF molecules. The most likely candidate for this common level is a CH(X) molecule with sufficient vibrational energy to cross into either the A or B state.

C_2 Emission

Excitation of the observed v' = 4 level of the Swan bands of C_2 requires 77.6 kcal/mole of energy. The only reasonable reactions that we have found for exciting this emission are

10) $C + C + M \longrightarrow C_2 + M$ $\Delta H = -141.6$ kcal/mole

11) $CH + CH \longrightarrow C_2 + H_2$ $\Delta H = -83.8$ kcal/mole,

and energy transfer from vibrationally excited HF. The reactions

12) $C + CH \longrightarrow C_2 + H$ $\Delta H = -60.6$ kcal/mole, and

13) $C + CH_2 \longrightarrow C_2 + H_2$ $\Delta H = -62.9$ kcal/mole

cannot excite v' = 4, but probably strongly contribute to producing ground state C_2.

The observation that C_2 emission peaks at an equivalence ratio of ca. 0.8 and falls off rapidly in the fuel-rich regime immediately eliminates a number of the above mechanisms from consideration. As discussed above, in lean flames carbon tends to be tied up as fluorine-containing radicals, and thus carbon atoms should be held to fairly low concentrations at low equivalence ratios. Thus reaction (10) cannot be primarily responsible for the Swan band emission. In addition, since reactions (12) and (13) are slow at low C atom concentrations, C_2 concentrations are also low in lean systems, making it unlikely that the Swan bands are excited by transfer of energy from vibrationally excited HF.

The only remaining mechanism, reaction (11), is in good agreement with all the observations. It predicts that C_2 emission increases as the square of the added CH_4, which is close to what is observed. As the flame becomes leaner, stripping from CH_3 radicals becomes less of a bottleneck, resulting in increases in CH concentration. In addition, as the flame is compressed, CH concentrations increase and Swan band intensity increases in both the fuel-rich and fuel-lean regime.

CHF Emission

There are a number of reactions that can provide the 63.5 kcal required to produce the highest emitting level observed in CHF. These are

14) $CH + F_2 \rightarrow CHF + F$ $\Delta H = -93.1$ kcal/mole

15) $CH_2 + F_2 \rightarrow CHF + HF$ $\Delta H = -127.7$ kcal/mole

16) $C + HF \rightarrow CHF$ $\Delta H = -75.3$ kcal/mole

17) $CHF + HF^* \rightarrow CHF + HF$

18) $F + CH + M \rightarrow CHF + M$ $\Delta H = -139$kcal/mole, and

19) $H + CF + M \longrightarrow CHF + M \quad \Delta H = -83.1.$

All these mechanisms predict the observed first- order dependence of CHF emission on added hydrocarbon at constant equivalence ratio. However, it is also necessary to rationalize the observation that, of the various emissions studied, that of CHF shows greatest persistence into the fuel-rich regime and that CHF emission intensity decreases with pressure. Both reactions (14) and (15) are very unlikely to predict such persistence, since in H_2-rich flames very little F_2 should survive past the infrared emitting region, while CH and CH_2 radicals should be formed slowly in the outer regions of the flame. With ground state (^3P) carbon atoms, reaction (16) should produce only triplet CHF, and not the emitting $^1A''$ state. $C(^1D)$ is thermodynamically accessible from the CH + F reaction, but its formation is 6 kcal endothermic from the CH + H reaction. Thus as equivalence ratio is increased, the production of $C(^1D)$ should fall off considerably. In the absence of a means of compensating for such fall off, reaction (16) must be considered an unlikely mechanism for populating CHF ($^1A''$). Reactions (18) and (19) should both strongly increase with pressure, since these are third order reactions at low pressures and F and H atoms only slowly combine in the post flame region. Elimination of mechanisms 14-16, 18 and 19, focuses our attention on reaction (17), vibration-to-electronic energy transfer from HF. Once again, this is most likely a multistep transfer through intermediate vibrationally excited states of CHF(X), facilitated by near coincidence between the vibrational frequency of HF and that of one of the modes of CHF. Highly excited states of HF are formed from the H + F_2 reaction, which in rich flames is complete close to the burner, and to a lesser extent from H + F atom combination, which occurs throughout the flame. CHF should be formed in increasingly poor overlap with highly vibrationally excited HF as equivalence ratio is increased. However, overall CHF concentrations may be increased by reaction (16) due to a reduction in the fraction of carbon that is tied up as fluorine-containing radicals.

The observed decrease in CHF emission with increasing pressure is explained as a result of three factors. First, CHF has a longer radiative lifetime than CH (2.45 sec for (000) of CHF[10] vs. 530 nsec and 360 nsec for the A and B states of CH[11]), and thus is more subject to quenching at higher pressures. Second, in the lean regime, ground state CHF is mainly formed by reactions such as (14) and (15), which decrease at higher pressures because the resulting higher temperature largely dissociates F_2 before it comes in contact with CH_2 and CH. In the fuel-rich regime, where vibrationally excited HF is separated from CHF due to the bottleneck reaction, increased vibrational relaxation of HF at higher pressure slows the rate of transfer of energy to CHF, much as has been discussed earlier for excitation of CH.

The proposed mechanisms for producing the emitting species provide interesting possibilities for diagnostics in fluorine-supported combustion. From reaction (11), the square root of the intensity of C_2 Swan bands is directly a measure of CH intensity (assuming a region of reasonably constant concentration can be isolated). Additionally, from reaction (5), $I_{CH}/[CH] = I_{CH}/(I_{C_2})^{1/2}$ should be a measure of the concentration of HF molecules with sufficient vibrational energy to result in electronically excited CH. This diagnostic could be employed in F_2-hydrocarbon combustion or in F_2-H_2 combustion that is doped with a trace of hydrocarbon. For propulsion systems, highly vibrationally excited HF in the exhaust represents wasted energy, in HF chemical lasers, vibrationally excited HF is the desired product of the combustion.

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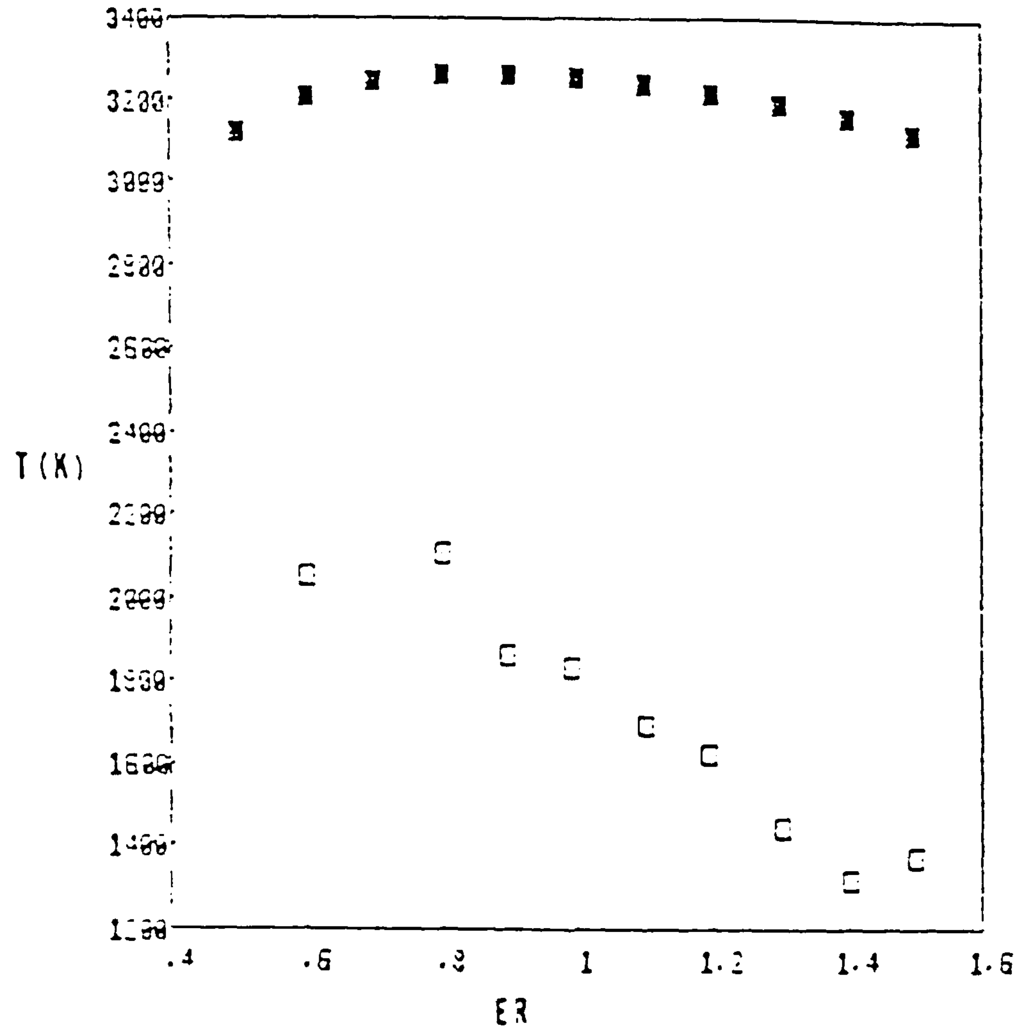

Figure 1. ⊡ -- Measured rotational temperature distributions in the HF (3-0) emission band in a H_2-F_2 flame at 7.7 Torr as a function of equivalence ratio.
■ -- Calculated adiabatic flame temperature of H_2-F_2 flame at 7.7 Torr

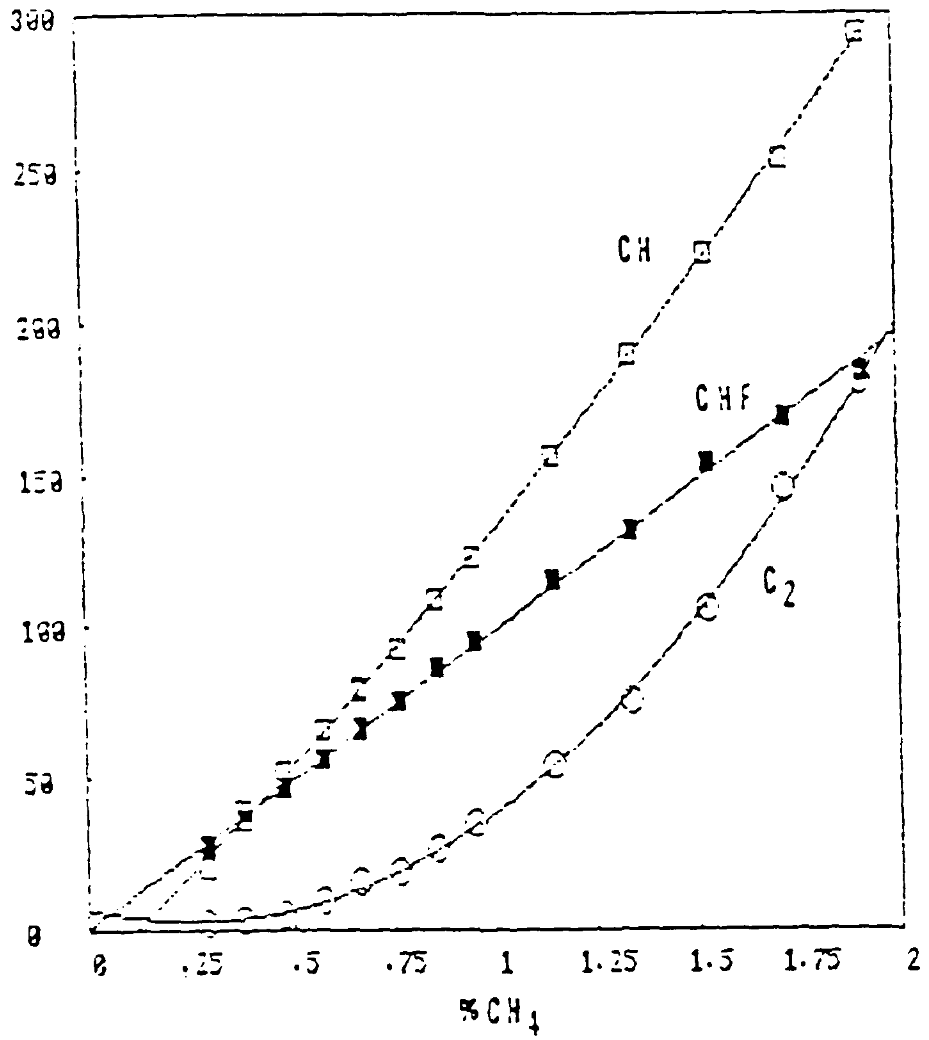

Figure 2. Emission intensity of CH (431nm), C_2 (516nm) and CHF (518nm) from $F_2/H_2/CH_4$ flames as a function of % CH_4 in fuel (Intensities of the different emissions are not comparable.)

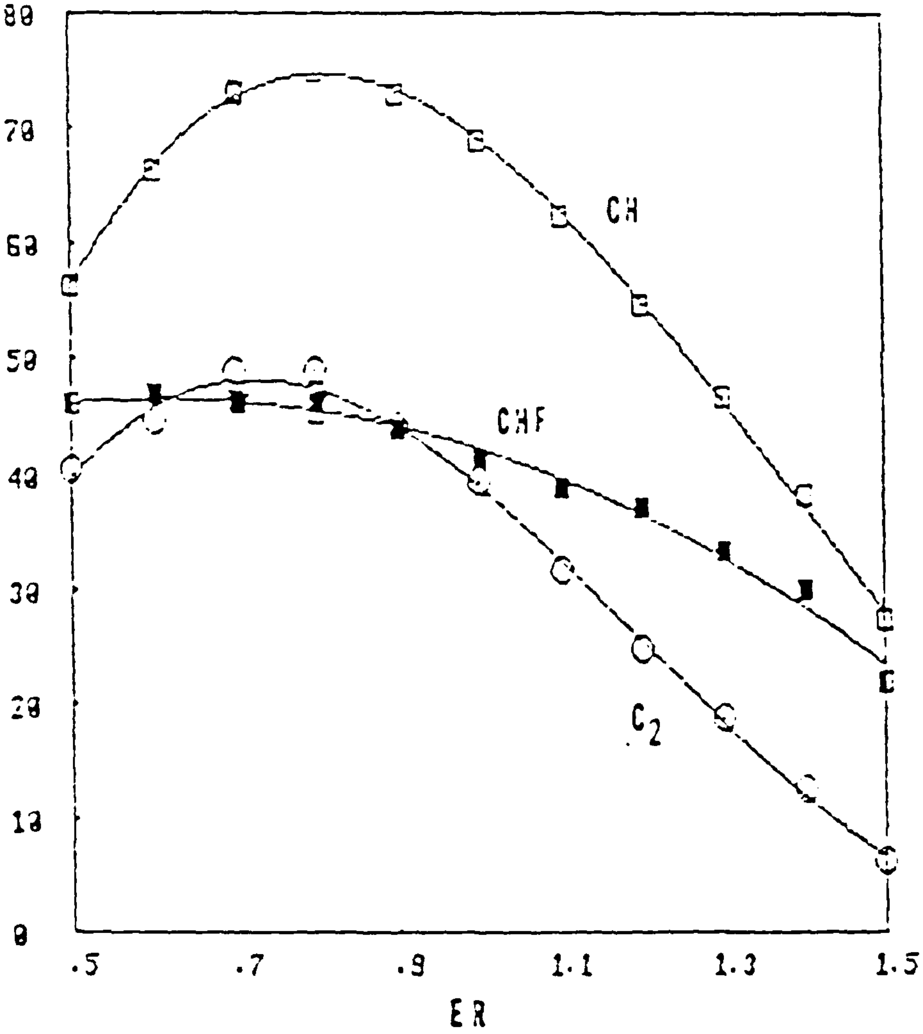

Figure 3. Emission intensity of CH (431nm), C_2 (516nm) and CHF (518nm) from $F_2/H_2/CH_4$ flames as a function of equivalence ratio (Intensities of the different emissions are not comparable.)

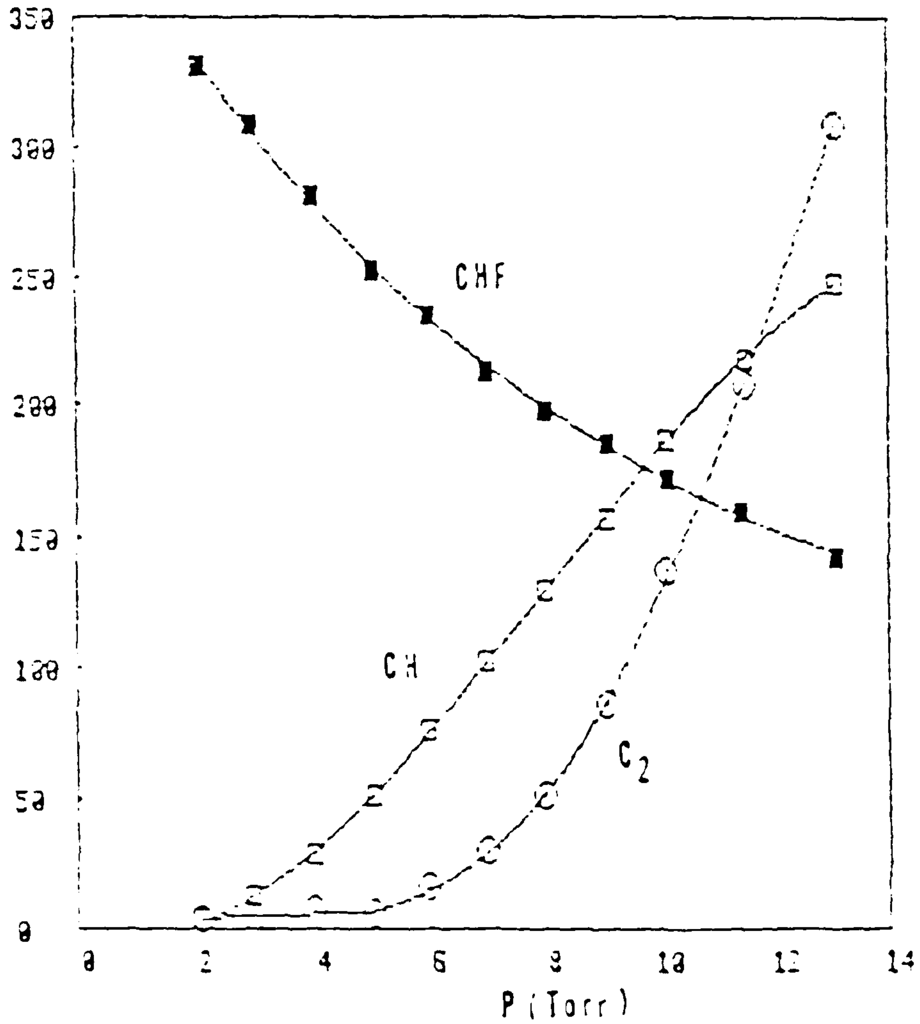

Figure 4. Emission intensity of CH (431nm), C_2 (516nm) and CHF (518nm) from $F_2/H_2/CH_4$ flames as a function of pressure (Intensities of the different emissions are not comparable.)

Luminescence from Dilute Methane-Fluorine Flames

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Besides the inherent interest of fluorine-supported combustion for lasers and advanced propulsion, such flames are also important for what they can reveal about combustion processes in general. Luminescence from CH and C_2 have been shown to be a common property of fluorine[1] and oxygen-supported[2] combustion of hydrocarbons. In the oxygen flames, decades of experimentation have not succeeded in establishing all the mechanisms producing these luminescences. If mechanisms for these emissions could be determined in fluorine flames, and if these mechanisms did not explicitly involve fluorine-containing species, the same mechanism might make a substantial contribution in oxygen combustion.

Notwithstanding their higher temperatures and burning velocity, fluorine flames are intrinsically simpler than oxygen flames. This is a result of fluorine being monovalent rather than divalent. There are no species analogous to peroxides and aldehydes to complicate fluorine-based combustion. Thus, mechanisms for light emissions can be more easily established in fluorine- than in oxygen-supported combustion. In addition, there are no multiple bonds to fluorine, forming compounds with bond strengths comparable to CO. Thus, if an emitting state is to be populated in a single reaction, there are usually fewer energetically feasible routes for producing the state in a fluorine flame than in the corresponding oxygen flame.

A very powerful method for studying mechanisms of luminescences in hydrocarbon flames is the method of very dilute flames. As applied to oxygen-supported combustion by van Tigglen and others[3], very small amounts of hydrocarbons were added to H_2-O_2 flames. In our studies, trace amounts CH_4 are added to H_2-F_2 flames. Addition of CH_4 at these levels does not appreciably change the basic flame parameters, such as flame temperature, burning velocity and the concentration of H and F atoms. Thus, the dependence of various luminescences exclusively on the concentration of hydrocarbon and carbon-containing radicals can be probed. Alternatively, the known variation of the properties of the H_2-F_2 flame as its equivalence ratio is varied can be used to study the dependence of the luminescence on the concentration of H and F atoms.

In addition to luminescence from CH and C_2 radicals, low pressure F_2-CH_4 flames also show emission from CHF radicals and highly vibrationally excited HF molecules. In the ultraviolet, emission from CF is observed. Under some conditions emissions from C_3, soot particles and impurity-derived OH are also detected. The various emissions show surprisingly large variations in relative intensity with changing flame conditions. In the present work, we systematically study the dependence of the intensities of CH, C_2 and CHF emissions on the parameters of H_2-F_2 flames containing very low concentrations of methane, with the aim of establishing the mechanisms for these emissions in fluorine combustion, and perhaps contributing to their understanding in other forms of combustion as well.

We have worked with slow-flowing (200-500 std. cm^3/min), dilute ($< 2\%$ CH_4), premixed H_2-F_2 flames at total pressures of 2-14 Torr. While adiabatic flame temperatures are about 3300 K for these flames, measured HF rotational temperatures are over 1000 K below this value, while HF vibrational temperatures are 600-1200 K above the adiabatic temperature. The dependence of CH, C_2 and CHF emission intensities on methane addition, equivalence ratio and total pressure are given in figures 1-3. Our preferred explanations for the observed variations are as follows:

CH emission is believed to be due to vibrational energy transfer between HF and CH. In rich flames this emission is reduced, since CH is formed only slowly, due to the "bottleneck" reaction, $H + CH_3 \longrightarrow H_2 + CH_2$, being much slower than the analogous $F + CH_3 \longrightarrow HF + CH_2$. As a result, in rich flames CH does not reach as high concentrations and exists in much poorer overlap with vibrationally excited HF than in lean flames . Observation of mainly CD emission from a dilute CD_4-F_2 flame is in agreement with the chosen mechanism. The only other energetically feasible reaction for producing CH emission, C + H combination, is not in accord with these observations. The ratio of emission intensities from the A and B states of CH is remarkably independent of flame conditions in these experiments, possibly due in part to facile collision-induced transfer between these states at flame temperatures.[4]

C_2 emission is explained as due to the reaction of two CH radicals, which explains its square dependence on added CH_4, its rapid dropoff in rich flames and its strong increase with increasing pressure, which compresses the flame and raises all concentrations.

CHF emission is also postulated to be due to vibrational energy transfer from HF, the fall off of this emission with pressure being partially due to quenching of the long-lived emitting state. This emission persists into the fuel-rich regime, since CHF (X) is in part formed by insertion of C atoms into vibrationally hot HF.

The proposed mechanisms suggest that $I_{CH}/(I_{C_2})^{1/2}$ should be a measure of vibrationally excited HF in each emitting region of H_2-F_2 flames dilute in hydrocarbon. Such a diagnostic could be used in HF combustion lasers, where vibrationally excited HF is the desired product, or in H_2-F_2 propulsion systems, where vibrationally excited HF in the exhaust represents wasted energy. Trace amounts of hydrocarbon would be added to these systems to generate the emissions for diagnostic purposes.

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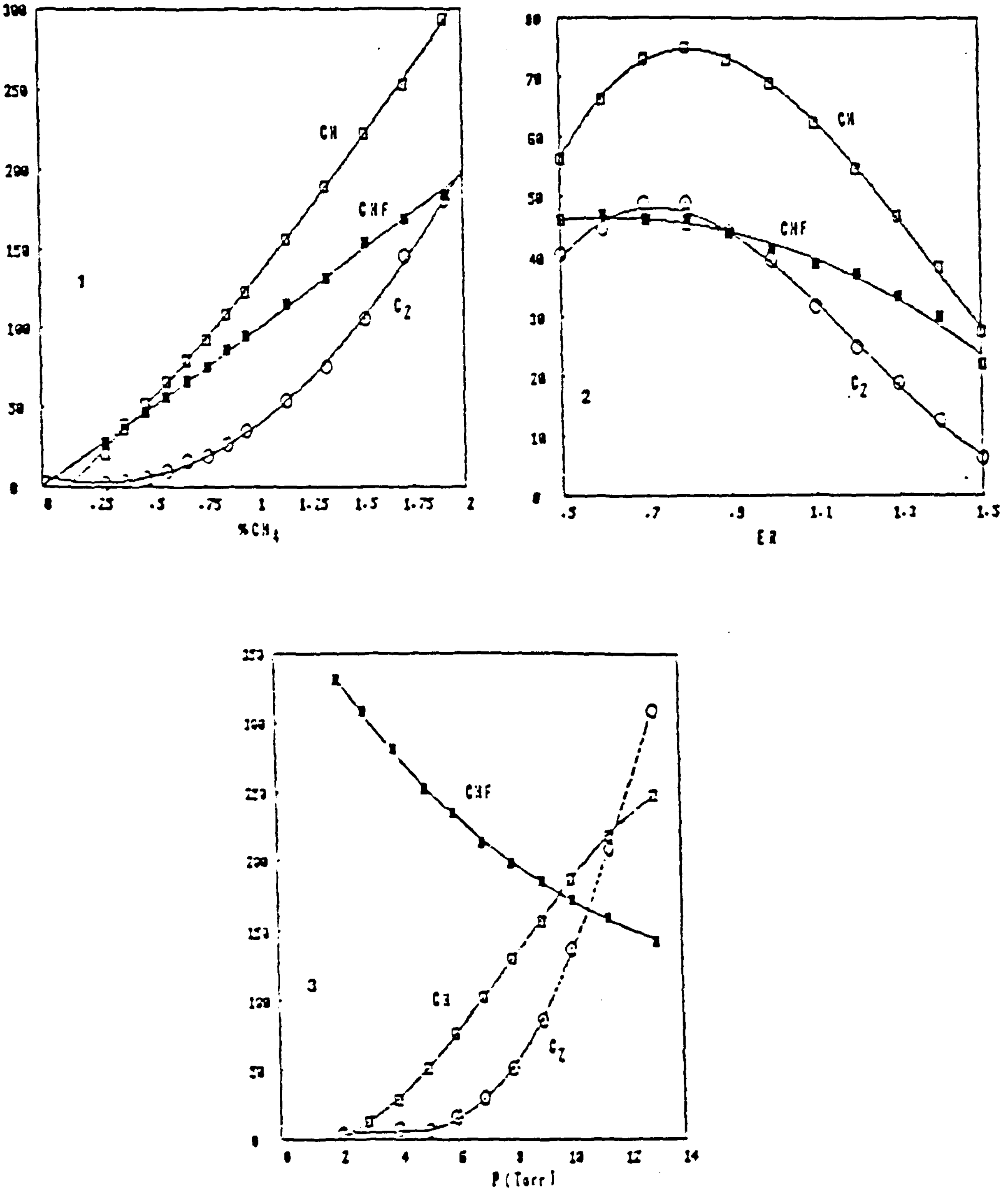

Relative emission intensity of CH (431nm), C_2 (516nm) and CHF (518nm) from $F_2/H_2/CH_4$ flames as a function of added CH_4 (fig. 1), equivalence ratio (fig. 2) and total pressure (fig. 3).