

AD-A188 818

COMBUSTION OF HYDROGEN AND HYDROCARBONS IN FLUORINE(U)
EMORY UNIV ATLANTA GA H KAUFMAN 15 SEP 67
AFOSR-TR-87-1985 AFOSR-84-0196

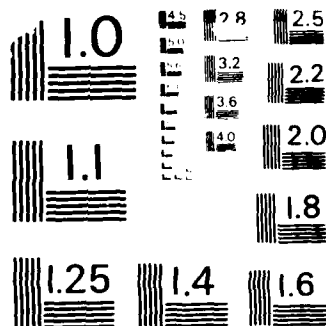
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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS - 1963

AD-A188 018 DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a REPORT SECURITY CLASSIFICATION Unclassified		1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY ELECTED		3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE JAN 14 1988		5 MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR-87-1905	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) H		5a NAME OF MONITORING ORGANIZATION AFOSR/NA	
6a NAME OF PERFORMING ORGANIZATION Emory University		7a NAME OF MONITORING ORGANIZATION AFOSR/NA	
6b ADDRESS (City, State, and ZIP Code) Atlanta, GA 30322		7b ADDRESS (City, State, and ZIP Code) Building 410, Bolling AFB DC 20332-6448	
8a NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR/NA		9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER AFOSR 84-0196	
8b ADDRESS (City, State, and ZIP Code) Building 410, Bolling AFB DC 20332-6448		10 SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO. 61102F	PROJECT NO. 2308
		TASK NO. A1	WORK UNIT ACCESSION NO.
11 TITLE (Include Security Classification) (U) Combustion of Hydrogen and Hydrocarbons in Fluorine			
12 PERSONAL AUTHOR(S) Myron Kaufman			
13a TYPE OF REPORT annual	13b TIME COVERED FROM 9/86 to 8/87	14 DATE OF REPORT (Year, Month, Day) September 15, 1987	15. PAGE COUNT 4
16 SUPPLEMENTARY NOTATION			
17 COSATI CODES		18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		fluorine, combustion, kinetics, CH, oscillation, titration, long-time	
19 ABSTRACT (Continue on reverse if necessary and identify by block number) In this program, low pressure flames of H ₂ and hydrocarbons burning in F ₂ are studied by measuring ionization, luminescence and laser-induced fluorescence of intermediates. Oscillatory and pulsing behavior are noted in these flames. Experiments are designed to establish the mechanism of CH A-state emission in oxygen-free combustion. Theoretical consideration of the long-time behavior of bimolecular reactions has provided a general endpoint indicator for chemiluminescent gas-phase titration reactions as well as a means of measuring rate constants for reactions such as H + F combination.			
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS		21 ABSTRACT SECURITY CLASSIFICATION Unclassified	
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Progress continues on both the experimental and theoretical aspects of our program. The work continues to yield information of fundamental importance to propulsion, combustion and chemical kinetics.

Theoretical Program

We have been exploring the long time behavior of bimolecular ($A + B$) reactions by both analytical and numerical methods. 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 ratio of reactant concentration, 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. The rate of reaction at long times varies by many orders of magnitude for small variations around the stoichiometric ratio of concentrations.

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 emitting products decay quickly, either radiatively or by quenching, chemiluminescent intensity is an instantaneous measurement of reaction rate. Fortunately, many reactions of interest in combustion and propulsion are chemiluminescent.

Analytical solutions for elementary bimolecular reactions show that measurements of chemiluminescent intensity as a function of the ratio of reactant concentration allows the determination of both the stoichiometric endpoint and rate constant of the reaction. The former 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 of reactions of importance in combustion and propulsion. If the reactive species (whose concentration cannot be directly measured) undergoes a chemiluminescent reaction with a stable species (whose concentration can be measured), the most "persistent" chemiluminescence indicates the endpoint of the reaction. The variation of light intensity around the stoichiometric point provides the rate constant of the reaction. This experiment is most simply arranged in a flow reactor, with

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chemiluminescence detector considerably downstream of the reagent mixing point.

Although the above results are interesting when applied to elementary bimolecular reactions, we have shown by both analytical and numerical methods that similar results are obtained for more complicated reaction mechanisms. Reactions in series and in parallel have been considered. The long time kinetic behavior of these systems has permitted the concept of "stoichiometric proportions of reagents" to be extended to systems in which this concept is not defined in an equilibrium sense. This work is presently being prepared for publication, and will be described in a forthcoming technical report.

These theoretical considerations of the long-time behavior of bimolecular reactions have a number of applications to our studies of fluorine-supported combustion. The theory provides an explanation of persistent emission that we previously have reported in studies of the $F + H_2$ and $F + CH_3OH$ reactions.^{1,2} In addition, a simple measurement of the $F + H$ recombination rate constant, an important datum for modeling F_2/H_2 propulsion systems, can be based on the theory.

We have proposed a model to explain nonsteady behaviors (oscillations and pulsation) that we have observed in a variety of fluorine-supported flames.³ 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. We are currently modeling the time dependence of these systems, using computer codes that can handle sets of reactions whose time constants vary over eight orders of magnitude. We have also 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.

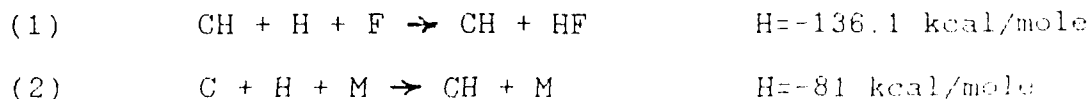
Experimental Program

We have received funding from the DoD University Research Instrumentation Program for a cw ring dye laser to be used in our fluorine combustion studies. This laser has been installed, and we are currently learning how to use laser-induced fluorescence (LIF) of I_2 for accurate

wavelength calibration of the system. The laser will be employed to monitor intermediates (eg. CH, C₂, CF and CF₂) in fluorine-supported combustion. A cw laser was chosen for our program in order to continuously monitor intermediates in oscillatory and pulsed combustion. In addition, since some of the intermediates of interest absorb in the ultraviolet, we have chosen a laser with doubling capabilities. In order to facilitate the application of laser techniques to our combustion program, the principal investigator attended the Gordon Research Conference on Physics and Chemistry of Laser Diagnostics of Combustion, at Plymouth, New Hampshire, during July 13-17.

Two experiments are underway in our low pressure flame burner. In one we are assessing the importance of nucleation on small ions as a source of soot in combustion, as has been proposed in a theory by Calcotte.⁴ The basis for our measurement will be the observation that observable ionization in fluorine-supported hydrocarbon combustion is completely eliminated when the ca. 1% oxygen impurity generally present in commercially prepared F₂ is removed.⁵ Thus by comparing soot formation in flames of hydrocarbons burning in commercial and purified fluorine, we are comparing systems with almost identical neutral chemistry but very different ion concentrations. Monitoring soot formation by infrared emission and laser scattering in F₂-CH₄ and F₂-C₂H₂ flames, we will compare both the soot-formation onset and the magnitude of soot formation in flames with purified and commercial fluorine.

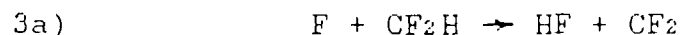
The second experiment being performed on our low pressure flame burner involves light emission from CH radicals, which is responsible for blue light often observed from the reaction zone of hydrocarbon flames. We have reported that CH A state emission is not dependent upon oxygen impurity.⁵ Since fluorine combustion chemistry does not involve the formation of double and triple bonds (such as those formed in CO₂ and CO in oxygen combustion), there are few reactions in combustion supported by purified fluorine that have sufficient energy to populate the A state of CH. The two most probable mechanisms are:



In order to compare the importance of these two mechanisms, we are monitoring CH emission while adding small amounts of methane to a H₂-F₂ flame. In these almost pure H₂-F₂ flames, the concentration of atomic fluorine and hydrogen

can be adjusted by manipulating the H_2/F_2 stoichiometry. The very different dependences of the rates of reactions (1) and (2) on these atomic concentrations will enable us to choose between these mechanisms. Ground state CH will be monitored in these flames by laser-induced fluorescence, and the dependence of CH A-state emission on CH ground state emission will be an additional criterion for choosing the predominant mechanism.

We have been attempting to measure the branching ratio of the



reaction. Reaction (1b) is a prototype for atomic displacement, which, if important in fluorine-supported combustion, could require that many additional pathways be considered in modeling these systems. Our initial attempts to make this measurement involved comparing hydrogen atom concentrations generated in the $F + CF_2H_2$ and $F + H_2$ systems by means of Lyman- α atomic resonance fluorescence. To date these measurements have not been successful, probably due to absorption of the Lyman- α radiation by HF product. Modifications are underway to increase the sensitivity of the detection system, so that lower concentrations of reagents can be employed in order to minimize absorption by HF. Alternatively, we will attempt to perform these measurements by using H + F recombination radiation as a means of monitoring H atoms in this system.

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