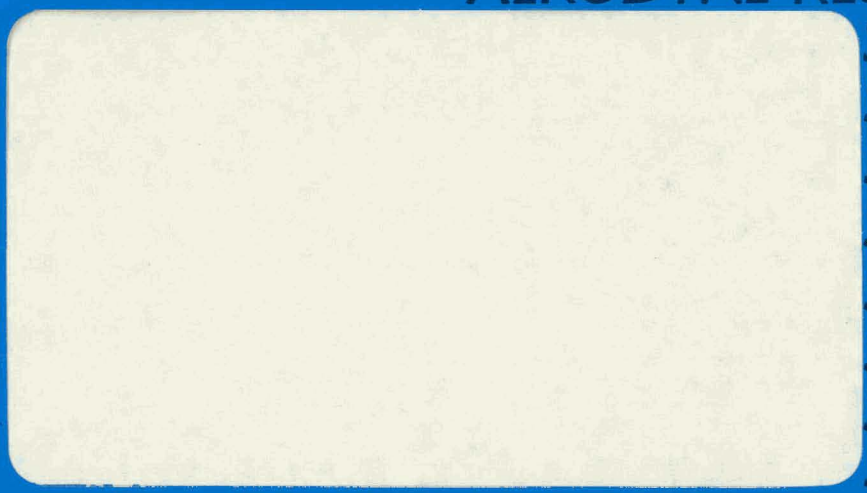

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FIRST QUARTERLY TECHNICAL PROGRESS REPORT ON A KINETIC STUDY OF NO_x FORMATION AND REMOVAL PROCESSES IN COMBUSTION STREAMS

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ABSTRACT

The production of nitric oxide from combustion of hydrocarbon fuels with air has been recognized to be a serious potential health hazard. In dirtier fuels such as coal and oil shale, a major source of nitric oxide occurs due to the reactions of small hydrocarbon fragments with the nitrogen in the air. These reactions take place in the rich part of the combustion flame and are termed the "Prompt-NO" mechanism. However, the detailed reaction sequence and rates of these reactions are not well known. The purpose of this work is to directly measure key reaction rates of the CH radical and subsequent HCN reactions which form the basis for Prompt-NO production. During this initial Quarter, production and detection methods for CH were devised and tested, and preliminary rate measurements made for the reaction of CH + N_2 at 300 K.

1. INTRODUCTION

The production of nitric oxide from combustion of hydrocarbon fuels with air has been generally recognized to be a serious potential health hazard for both indoor and outdoor environments.[1-3] Even with clean fuels such as natural gas, nitric oxide is generated from the reactions of the flame species with nitrogen in the air. In dirtier fuels, such as coal and oil shale, additional nitric oxide is produced from bound nitrogenous species. Two distinct processes lead to the formation of NO from N_2 in the combustion air: the slow oxidation of N_2 by oxygen containing species (Zel'dovich mechanism[4]) and the reactions of N_2 with hydrocarbon radicals whose products are subsequently oxidized to NO ("Prompt-NO").[5] The former process is thought to be well understood but the details of the latter are poorly known, despite its importance in NO_x emissions. The goal of this program is to develop a detailed understood, of the prompt NO mechanism by direct measurement of the temperature dependent rate coefficients and product branching ratios for selected key reactions. These reactions may be significant in the formulation of various NO_x or combined NO_x/SO_x control schemes in two ways. First, by better understanding the reactions relevent to NO formation, one might be able to more intelligently design combustion modifications, such as those used in staged combustors. In current designs, the first stage runs under fuel rich conditions so that more of the fuel-nitrogen is converted to N_2 rather than NO. However, this could increase the production of prompt NO, partially offsetting the advantage of staging. Secondly, these reactions could conceivably be used to advantage in a post-combustion NO_x reduction scheme, similar to that used in the thermal deNO_x process, where gaseous ammonia injected into the exhaust gas flow selectively reduces NO to N_2. Cleanup methods of this type will be most useful only with a comprehensive knowledge of the detailed chemical mechanisms involving nitric oxide.

1.1 Review of Prompt NO Formation

1.1.1 NO_x Production Mechanisms in Hydrocarbon Combustion

The formation of NO_x in flames may arise either from N_2 in the combustion air or from nitrogen species contained in the fuel. Fuel nitrogen can be the main source of NO_x emissions in combustion systems, for example those utilizing certain coals or the products of coal gasification[4]. Here, the bound nitrogenous species are rapidly converted to small intermediates such as NH, NH_2, CN, and HCN. In fuel rich regions, N_2 is rapidly formed. All of these species, including H_2, may lead to the formation of nitric oxide. In many instances, practical combustion systems utilize fuels, such as natural gas, which are relatively free of nitrogen-containing species. Understanding the production of NO_x from atmospheric N_2 in these systems is also important.

Two mechanisms for formation of NO_x from combustion air in hydrocarbon-air flames have been generally identified.[6] These mechanisms are the thermal oxidation of N_2 through attack by oxygen atom radicals, and an apparent second mechanism (termed the "prompt NO" mechanism)[5] which is thought to arise from reaction of hydrocarbon fragments with molecular nitrogen. The thermal oxidation of N_2 in flames and post-flame gases occurs by the extended Zel'dovich mechanism.[4]

$$O + N_2 \rightarrow NO + N \qquad (1\text{-}1)$$

$$N + O_2 \rightarrow NO + O \qquad (1\text{-}2)$$

$$N + OH \rightarrow NO + H \qquad (1\text{-}3)$$

The mechanism is well understood, although some uncertainty may persist in knowledge of the reaction rate for the rate-determining step, Reaction (1-1). Production of NO through this mechanism is highly dependent on combustion conditions (flame temperatures, O atom concentrations, turbulent mixing and post-flame residence time) but does not depend directly on the composition of fuel. Various techniques to minimize thermal NO_x production, such as staged

combustion, or burning in low excess air to starve the O atom concentrations, have met with some measure of success.[6]

Despite the general agreement on the Zel'dovich mechanism, a number of studies of hydrocarbon combustion in various environments (including laminar premixed flames and turbulent diffusion flames) have shown NO concentrations in excess of predicted levels which are based on the extended Zel'dovich mechanism.[6] A study of NO formation by Fenimore[5] in laminar premixed flames of ethylene, methane, or propane burning in N_2-O_2 mixtures suggested a rapid transient formation of NO in the primary reaction zone. The formation of this "prompt NO" appeared to require hydrocarbon fuels and occurred at small O atom concentrations such that the Zel'dovich mechanism would not account for the apparent NO formation rates in the primary reaction zone. Fenimore[5] proposed that the prompt NO formation could be due to reaction of hydrocarbon fragments, such as CH, CH_2, or C_2, with molecular nitrogen to form HCN or CN, with subsequent oxidation of these species to NO.

The question of the existence of prompt NO has been the subject of controversy. The initial studies by Fenimore[5] did not actually probe the primary reaction zone, and the presence of prompt NO was inferred by extrapolation of measured axial profiles to the burner head, where a nonzero [NO] intercept was obtained. An alternative suggestion of Sarofim and Pohl[7] from studies in premixed laminar CH_4-air flames was that, except possibly in very fuel-rich flames, the formation of prompt NO in the flame zone could be explained on the basis of the Zel'dovich mechanism, assuming O atom concentrations in substantial excess of equilibrium.

In more recent flame studies, measurements of local O atom concentrations and temperature profiles in the primary reaction zone, in combination with kinetic modeling, have shown that the Zel'dovich mechanism is not adequate to account for observed rates of NO formation.[8] A study by Hayhurst and Vince,[9] in which trace amounts of hydrocarbons were added to the gas mixtures for premixed H_2-O_2-N_2 flames, showed significant and unambiguous increases in the sampled NO concentrations as hydrocarbons were added. In addition, the

incremental yield of NO (prompt NO) was found to be proportional to the number of carbon atoms in the parent hydrocarbon. Other indications of the existence of a non-Zel'dovich prompt NO mechanism have been found in well-stirred reactors[10] and in turbulent diffusion flames.[11] Based on these various observations, the concept of a mechanism for NO production in hydrocarbon combustion which is distinct from the Zel'dovich mechanism appears to have received general acceptance.[6]

The practical importance of prompt NO as a pollutant in actual combustion systems will of course depend on fuel type as well as combustion conditions. The premixed flame studies generally show that the occurrence of prompt NO is not very temperature dependent, and it is not strongly dependent on stoichiometry under fuel rich conditions, although the prompt NO levels are much lower in lean flames.[6] Since practical flames are in general not premixed, and may be turbulent, reaction zones which are at least slightly fuel-rich are to be expected in most combustion systems. The prompt NO mechanism can therefore be a potential source of significant NO_x emissions in most situations where "clean" (containing insignificant fuel nitrogen) hydrocarbon fuels are burned as well as for "dirty" fuels burned under fuel rich conditions.

1.1.2 Kinetic Mechanisms for Prompt NO Formation

Although complete understanding of the detailed reaction steps is lacking in a description of prompt NO formation from hydrocarbon combustion, three stages in the process are generally recognized.[6] The first stage is the production of cyano type intermediates (HCN, CN, C_2N_2), as well as N or NH, by reaction of hydrocarbon fragments (CH, CH_2, C_2, etc.) with N_2. In the second stage, the HCN or CN is converted to NH_i by other flame species, and finally the NH_i species are converted in part to NO. The mechanisms pertaining to HCN destruction and conversion of NH_i species to NO are also relevant to NO_x production from fuel nitrogen. The goal of this program is to obtain direct measurements of the temperature-dependent rate coefficients for key reactions in both the HCN formation and destruction steps. These measurements would be combined with experimental and modeling results from recently

completed studies of NH_i-NO_x reactions and mechanisms at Aerodyne to provide a more complete and detailed description of NO_x formation during combustion.

2. PROJECT STATUS REPORT

September 15, 1982
Report No. ARI-RP-114
Report Period: 8 June 1982 - 31 August 1982

CONTRACT TITLE AND NUMBER:

A Kinetic Study of NO_x Formation and Removal Processes in Combustion Streams
DE-AC21-82MC19028

CONTRACTOR NAME: Aerodyne Research, Inc.
45 Manning Road
Billerica, MA 01821

CONTRACT PERIOD: 8 June 1982 - 8 October 1983

1. Contract Objective: No Change

2. Technical Approach Changes: No change to technical approach.

3. Contract Tasks:

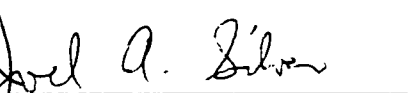
   Task 1 - Source and Detection Techniques for CH. This task was completed during this period. CH is produced by mixing a slight excess of atomic fluorine (made in a microwave discharge) with methane. It is detected using laser induced fluorescence at 429.8 nm in the $X^2\Pi - A^2\Delta$ electronic band.

   Task 2 - Rate Measurements. Room temperature measurements for CH + N_2 were made and agree well with previously reported values. Detailed analysis (flow correction) routines were set up so that the results will be as accurate as possible.

   Task 3 - Evaluation of existing Data. A comprehensive literature search has been performed for all chemistry relevant to the formation of prompt NO and is currently being evaluated.

4. Open Items: None.

5. Summary Status Assessment and Forecast: This is the first quarterly report for this contract. The work is progressing on schedule and the temperature dependent rate constants for $CH + N_2$, NO, and NO_2 will be measured during the coming quarter.



J.A. Silver, Program Manager

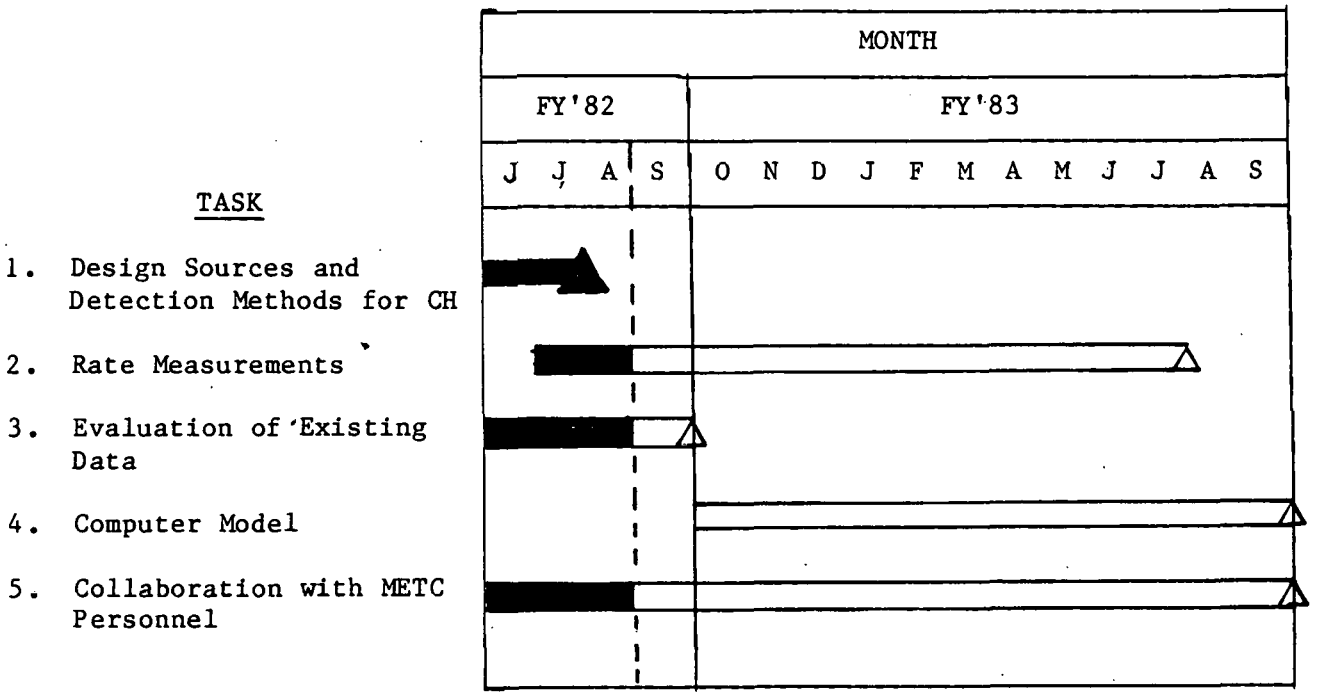


Figure 2.1 Contract Task Schedule

3. PRODUCTION AND DETECTION OF CH

3.1 Task Goals and Milestones

The purpose of this task is to develop a suitable source of CH radicals for use in the Aerodyne high temperature fast flow reactor. In addition, this task requires the development of a sensitive method for detecting CH. These goals have been achieved, using methods largely developed at METC for production of CH from the stripping reactions of F + CH_4, and for detection using laser induced fluorescence.

3.2 Technical Discussion

3.2.1 CH Production

The reaction of atomic fluorine with hydrogen containing molecules often results in a rapid abstraction to produce HF plus the remaining radical. This approach has been used successfully to cleanly produce NH_2 from the reaction of atomic fluorine with excess ammonia.[12,13] Using this method, we mixed moderate excesses of atomic fluorine, produced in a microwave discharge in excess helium carrier gas, with methane. The admixture of these species occurs in a coaxial inlet tube arrangement, shown in Figure 3.1, which permits the CH formation reactions to reach completion before being admitted into the 75 cm long, 7.26 cm dia. flow tube. This flow reactor is fully described in Ref. 14 and will not be discussed further. If CH_4 is added via the moveable injector rather than through the outer coaxial inlet tube, visible chemi-luminescence can be observed (with the injector near the viewing port). Near optimum mixing ratios of F_2 and CH_4 were obtained by "tuning" this flame until a deep blue color developed, characteristic of CH. This is a cruder approach than the more elaborate OMA techniques used by Nesbitt[15], but serves as a good way of initially making some CH so that the laser may be properly tuned and fluorescence optimized. Once CH was detected, the methane was switched back

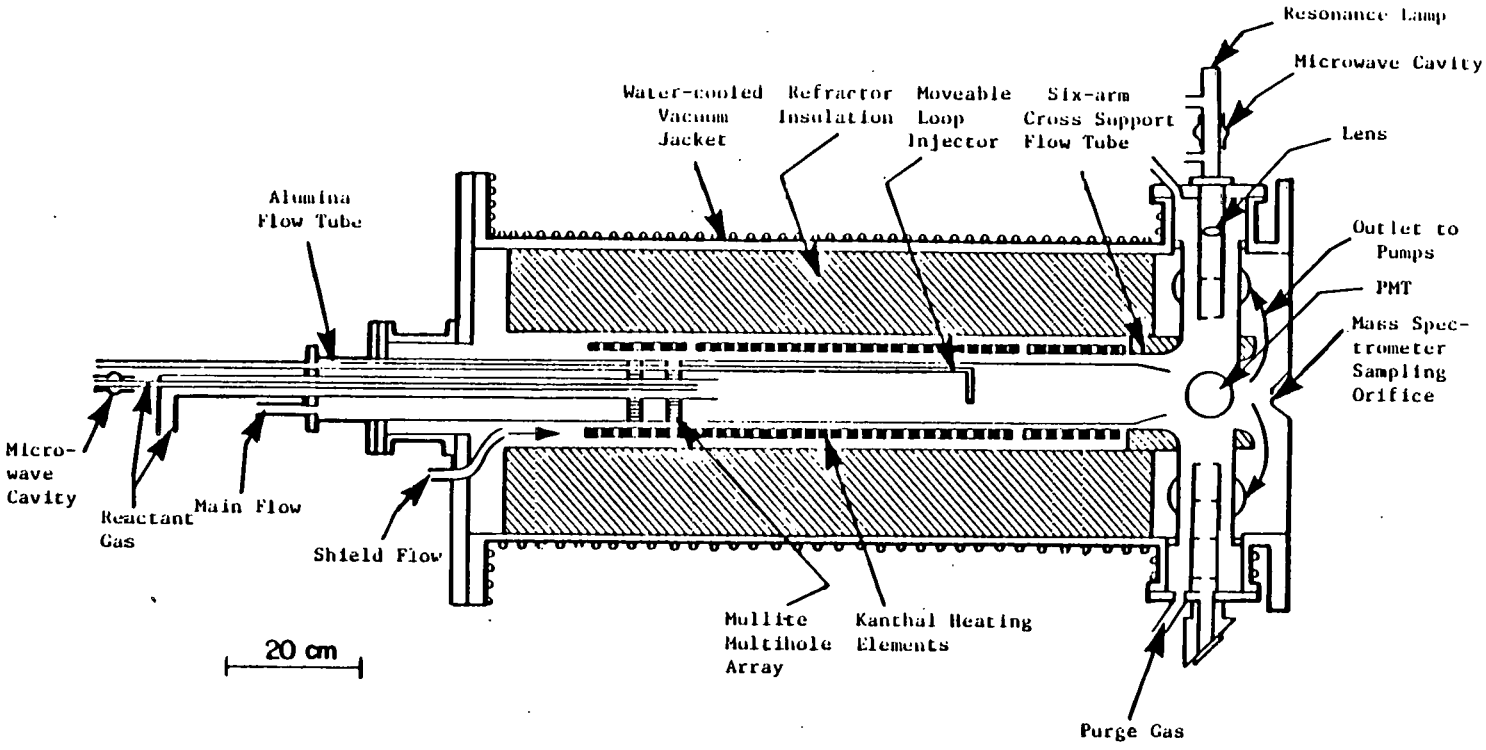


Figure 3.1. Aerodyne High Temperature Flow Tube Reactor.

to the coaxial inlet tube and the mixtures optimized. It appears that a F_2/CH_4 ratio of ~3-4 works best. Unlike the formation of NH_2, this mechanism involves sequential hydrogen atom abstraction and, in all likelihood, produces a host of small radical species in addition to CH, at similar concentration levels. As long as the reactant gas concentration is kept in excess of [CH], i.e. pseudo first order kinetic conditions are maintained, this presents no problem for making rate measurements.

3.2.2 CH Detection

Using the $X^2\Pi(v'' = 0) \rightarrow A^2\Delta(v' = 0)$ electronic band near 431 nm, CH was detected by laser induced fluorescence. A nitrogen pumped dye laser (Molectron UV14 and DL14, respectively) produces 200 μJ pulses which excite lines in the A-X transition. The unfocused laser beam is steered through the detection region and is collimated by a set of black anodized baffles. Fluorescence is imaged through an f/1.5 lens and interference filter (λ_0 = 428.6 nm, FWHM = 7.3 nm) into a gated photomultiplier tube (Hammamatsu R763P). The signal is integrated, amplified and transmitted to a PRIME 400 computer for on-line analysis. Averaging, background subtraction and normalization to the laser pulse energy are done by the computer.[16] The laser frequency is also computer controlled and can automatically scan or find the center of an excitation line. A sample excitation spectrum of CH from 428.5 - 431.5 nm is shown in Figure 3.2. The most intense line, hence the one used for all further rate measurements described in this report, is the $R_1(2)$ unresolved doublet of the ($v' = 0 \rightarrow v'' = 0$) transition at 429.8 nm.[17] It is estimated that the detection sensitivity using this technique is ~10^6 molecules cm^{-3} for 100 laser pulses with a S/N = 1.

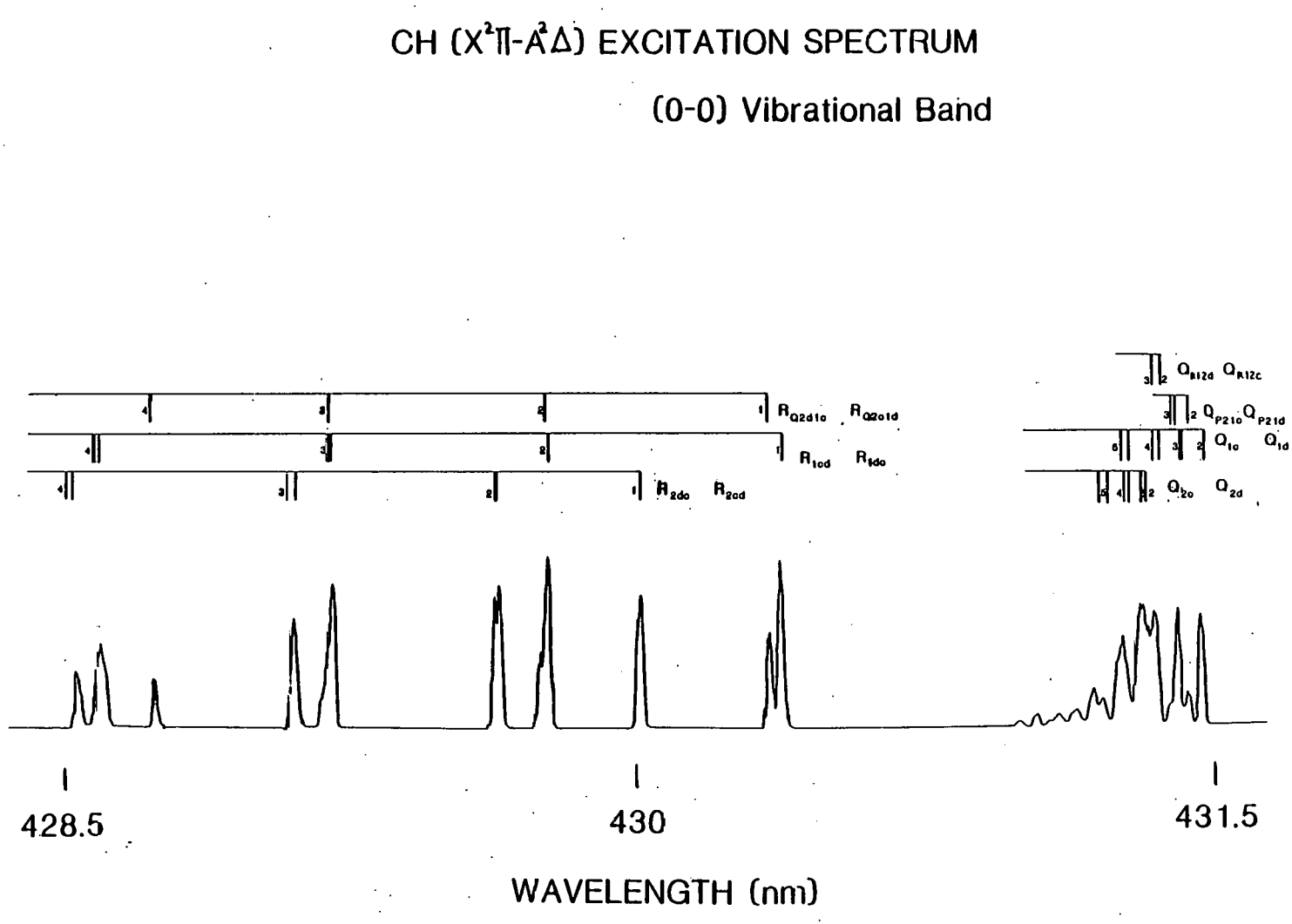


Figure 3.2. CH Excitation Spectrum.

4. REACTION RATE MEASUREMENTS OF CH

4.1 Task Goals and Milestones

The purpose of this task is the direct measurement of suspected key reactions involved in the formation of NO in combustion flames. Foremost among these is the reaction of CH with N_2, thought to be the initiation step for the formation of Prompt-NO. The reaction of the HCN product with atomic oxygen and the hydroxyl radical are also of interest. In addition, NO and NO_2 might be removed via reaction with CH. The temperature dependent rate constants and product channels for these reactions are to be measured in the ARI high temperature fast flow reactor as part of this task. At this point in time, room temperature measurements of CH with N_2 have been performed, and the system has been prepared to extend the N_2 measurements (as well as do CH + NO and NO_2) to higher temperatures.

4.2 Technical Discussion

4.2.1 Heterogeneous (Wall) Removal of CH

Before measuring any rate constants, one must determine the extent to which CH is removed by reactions with the flow tube wall. The value of the first order wall removal rate (k_w) is needed to accurately analyze the observed reaction rate to produce the "true" rate; i.e. - a value corrected for diffusional effects. Since the rate measurements use a fixed CH source, all decays are independent of k_w to first order, but show a varying degree of dependence to k_w with application of the diffusion corrections.[13,18]

These measurements are made by varying the flow velocity (residence time in the tube) at fixed pressure (diffusion). A plot of ln (signal x velocity) vs. 1/velocity produces a straight line whose slope equals $k_w z$, where z is the distance from source inlet to the detector. The observed k_w for CH in

1.8 Torr of helium with an uncoated alumina wall (radius = 3.63 cm) is ~200 s^{-1}, as shown in Figure 4.1. This corresponds to a γ (wall sticking coefficient) of ~.021

$$k_w(s^{-1}) = \frac{\gamma \bar{c}}{2r} \qquad \bar{c} = \text{mean molecular speed} \qquad (4.1)$$

This value is reasonably high and results in a rapid loss of CH concentration as it flows down the tube. The insertion of a Teflon liner in the flow tube lowers k_w to 85 s^{-1} (radius = 2.97 cm), resulting in $\gamma \approx .007$, an improvement of a factor of three. This is significant, since the CH concentration depends exponentially on k_w. Unfortunately, we cannot use this liner for the high temperature studies and will have to work with a large k_w. To accommodate this fact, we have reanalyzed the flow correction formulas of Brown[18] and significantly extended the regions of validity of his program to include higher values of k_w and lower diffusion coefficients.

4.2.2 Reaction Rate for $CH + N_2$ at 300 K

The reaction rate constant for $CH + N_2$ has been the subject of a number of studies at room temperatures[15,19-24] and in a flame.[25] The room temperature rates vary by over an order of magnitude and are much higher than would be expected from extrapolating the flame data to room temperature. It has been suggested[21,22] that this reaction has two pathways,

$$CH + N_2 \rightarrow HCN + N \quad \text{(high T), and} \qquad (4.2a)$$

$$\xrightarrow{M} HCN_2 \qquad \text{(low T)} \qquad (4.2b)$$

This would explain the differences in measured room temperature rates, since they were originally performed at different pressures. Wagal, et al.[22] measured this reaction over a large range of pressures and determined that the

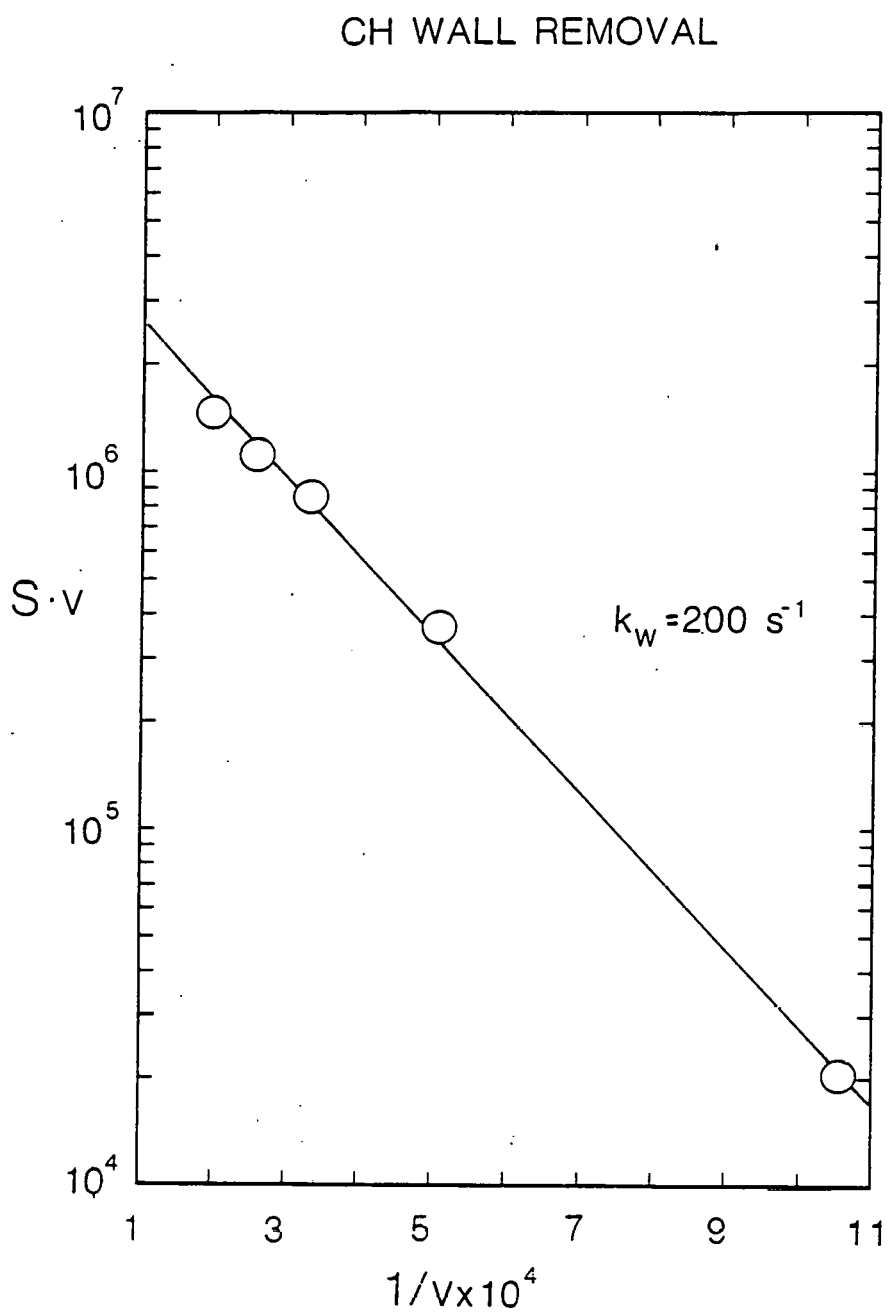


Figure 4.1. Wall Removal Measurement for CH in Flow Tube.

termolecular k(low pressure limit) = (2.6 ±0.3) x 10^{-31} cm^6 $molecule^{-2}$ s^{-1} and the bimolecular high pressure limit rate constant is ($p \rightarrow \infty$) equal to (6.3 ±1.3) x 10^{-13} cm^3 $molecule^{-1}$ s^{-1}. Berman et al.[26] recently reported measuring a slight negative temperature dependence over a limited temperature range.

As a first step in our extending these studies to T > 1000 K, a room temperature measurement was made. Because of the small rate and large k_w, the amount of N_2 required was fairly high; thus, it was added along with the main flow gas (helium) rather than through the moveable injector. The resultant rate, corrected for k_w and diffusion, is 2 x 10^{-31} cm^6 $molecule^{-2}$ s^{-1}. The estimated error of this preliminary results is ±50%, but agree quite well with the value of Wagal.

4.2.3 Work Forecast

This task has just begun and, during this next quarter, we should obtain the temperature dependent rate constants for the reactions of CH with N_2, NO, and NO_2. In addition, the necessary equipment and gases needed to measure the rates of HCN with O and OH will be ordered and assembled.

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