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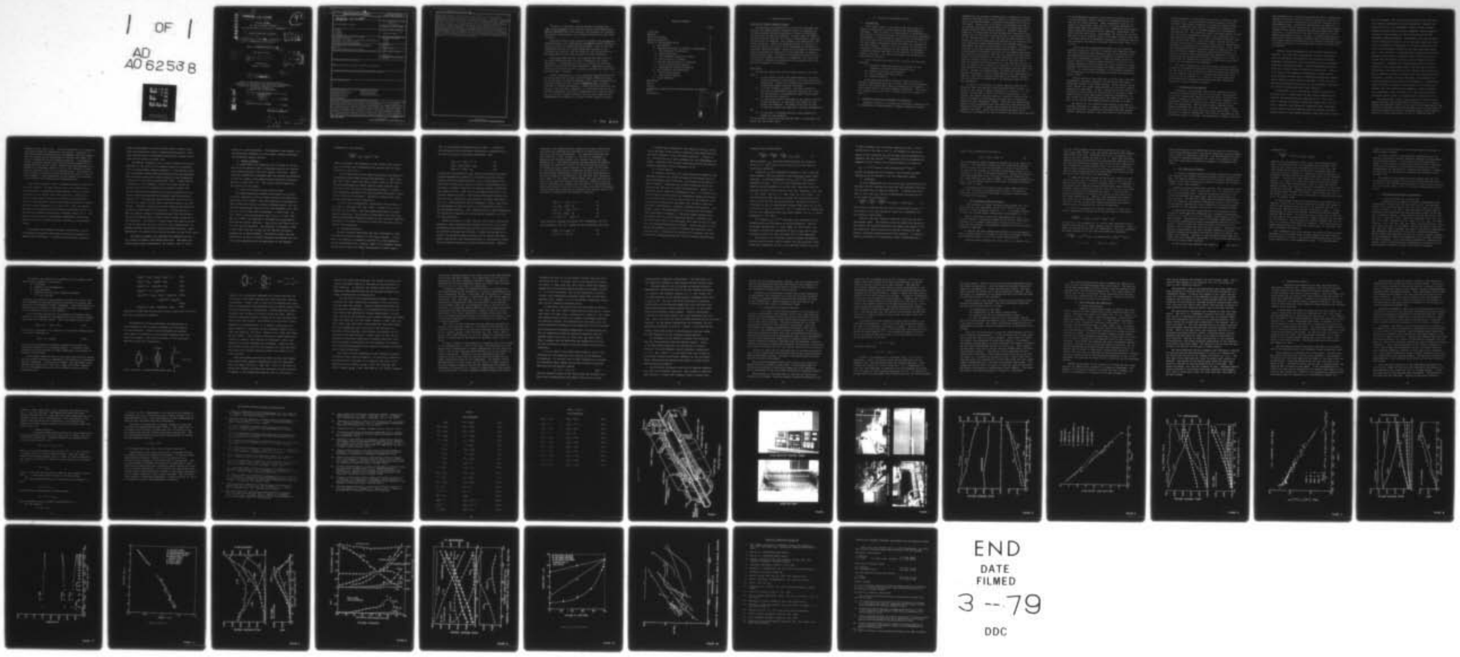

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Interest in chemically related combustion problems has lead to an integrated fuels research program under AFOSR support. Research emphasis is on the pyrolysis and oxidation of aliphatic and aromatic hydrocarbons, soot formation/destruction and carbon oxidation. Detailed results on the pyrolysis of ethene and propane are presented herein, and a review and analysis of aromatic oxidation giving insights into mechanisms are reported. Data on the high temperature oxidation of toluene have been obtained on the Princeton flow reactor, and the oxidative rate characteristics have been observed to differ markedly from the aliphatics.
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Experiments dealing with the formation and destruction of soot have been undertaken from both fundamental and overall approaches. A comprehensive review and analysis of practical results of inhibitors has been undertaken. Experiments aimed at exploring the importance of OH radicals introduced by water addition have been initiated. Overall experiments utilizing apparatus developed during the current program have pursued the measurement of sooting height as an indication of sooting tendency. Soot height characteristics of several fuels and fuel mixtures have been made including mixtures of toluene and heptane. A second approach involving premixing of fuel and soot inhibitors in a diffusion flame burning has been considered, and initial experiments are currently underway. A review of carbon oxidation has also been completed and preparations are underway to initiate carbon oxidation studies.

ABSTRACT

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I. Research Objectives

Abstract of Overall Research Effort

Recognizing the uncertainities as to future available fuel sources, the AFOSR supported research effort at Princeton has now been directed towards establishing a center of excellence in combustion related fuel problems. Current areas of endeavor include oxidative pyrolysis of aliphatic hydrocarbons, pyrolysis and oxidation of aromatics, soot formation and destruction, and carbon oxidation. Other fuel combustion areas of interest to Princeton and the Air Force will be undertaken as the center of excellence develops further. Efforts with respect to hydrocarbon kinetics represent an extension of work undertaken in earlier AFOSR supported work. From this work important overall rate expressions for combustion modelling, fundamental rate data, and key chemical insights were obtained by the extensive use of the Princeton turbulent flow reactor.

Objectives

The specific objectives of the current contract year have been:

(1) to gain better insight and understanding as to hydrocarbon pyrolysis in the presence of various oxygen concentrations. During this current year studies involving propane and ethene have been undertaken

(2) to review aromatic oxidation, initiate a series of qualitative experiments using the turbulent flow reactor and develop in an operational mode a GC/MS system for quantitative analysis.

(3) to review the state of knowledge of the general features of soot formation, in particular the effect of inhibitors and promoters. Analysis of the role of water on the soot process has also been a central consideration.

and

(4) to initiate a literature search on the oxidation of carbon at high pressure.

All of the above objectives have been met and, in some areas, exceeded for the current year.

II. Status of the Research Effort

A. Introduction

This annual report is the first since the concept of a center of excellence in fuels research was established at Princeton. Thus, we think it is appropriate to concentrate on the efforts in progress and the new initiatives being considered. Consequently, in this section we will not give an extensive review and history of our previous efforts and results, nor list the over eighty publications which have been the outgrowth of our AFOSR support. However, we will continue our practice of listing all published material by the program investigators in a reference section and refer to this material by reference number in the text. All other references will be explicitly identified in the text.

In the following sections we shall discuss the following programs:

(1) aliphatic hydrocarbon pyrolysis kinetics in the presence of various oxygen concentrations
(2) aromatic pyrolysis and oxidation
(3) soot formation and destruction
(4) carbon oxidation

In the next section which primarily covers the work on aliphatic hydrocarbon pyrolysis, we will give a brief conceptual review of the hydrocarbon kinetics program and the turbulent flow reactor used in the Fuels Research Laboratory. This review will relate not only to Item (1) above, but also to Items (2) and (3).

B. Combustion Kinetics of Aliphatic Hydrocarbons

Numerical modelling is playing an increasingly important role in forwarding our understanding of complex combustion systems.

Consequently the accurate representation of combustion kinetics becomes a necessary and critical element in advancing analytical tools to guide development of hardware compatible with alternative fuels. Recent work at Princeton and elsewhere has led to an improved conceptual understanding of high temperature hydrocarbon pyrolysis and oxidation chemistry. However, detailed modelling of hydrocarbon reaction systems more complicated than methane has not been wholly successful due to the complex nature of the chemical kinetics. Both the lack of understanding of the elementary reaction mechanisms and availability of accurate rate data required to model these systems over extended ranges of temperature and pressure contribute to the problem. Furthermore, although it has been frequently demonstrated that relatively large systems of elementary reactions can be handled numerically, the numerical complexities and code size required to model real energy conversion systems, even with simplified fluid mechanical coupling, remain prohibitive. Thus much of the modelling to date has employed some approximation to the chemical kinetics in order to predict the interaction of chemistry and fluid mechanics which determine the energy release distribution and pollutant formation. Through its AFOSR support, Princeton has pioneered in determining realistic kinetic approximations for hydrocarbon combustion. This work, generally referred to as overall (global) reaction kinetics, is summarized in an extensive paper by Dryer and Glassman(1).

In reality, this insight to global reaction kinetics was developed from the excellent, detailed experimental results obtained on the unique Princeton turbulent flow reactor (2). The reactor is described in detail in the next sub-section. The present flow reactor has the ability to spread a reaction over a spatial distance of approximately one meter and to operate at relatively high temperature (1400K). Thus detailed steady-state sampling can be performed with high resoltuion and free from the effects of diffusion of species and temperature since all spatial gradients are small. From the concentration-distance (time) profiles it is possible not only to observe the qualitative features of the hydrocarbon pyrolysis and oxidative processes, but also to quantitatively identify important intermediate species as well as all stable products. These intermediates may not be crucial to the overall rate, but are of extreme importance in identifying under what conditions (e.g. temperature and stoichiometry) possible pollutants such as oderants, carcenogens, and soot could and would form. Furthermore, the quality of the data has been of such a precise nature, that under suitable conditions it has been possible by deductive reasoning to determine reaction rate constants for several elementary reaction steps (Refs. 2,3, 4,5,6,7).

One of the major experimental results in the Princeton kinetics program (8) has been to identify that modelling alkane combustion chemistry over-extended ranges of equivalence ratio and temperature requires the consideration of sequential but partially overlapping processes. These processes include: an initial period of induction phase chemistry; conversion of the primary alkanes to olefins; oxidation of the olefins to carbon monoxide and finally the oxidation of carbon monoxide to carbon dioxide. The simultaneous oxidation of the hydrogen produced in the destruction of the hydrocarbon overlaps the latter three steps as well.

Similar studies of the pyrolysis of alkane fuels have been performed to elucidate important initiation and fuel radical mechanisms present in pyrolysis systems. These studies provide great insight into oxygen catalyzed and rich oxidation studies subsequently undertaken. A later sub-section of this section is devoted to recent studies of the pyrolysis of aliphatic hydrocarbons both in inert and slightly oxidizing atmospheres. In the context of the above description the importance of this effort to the overall hydrocarbon oxidation process is evident.

The ability of the turbulent flow reactor to provide precise data resolved on a spatial (time) coordinate was, of course, a motivating factor in proposing to approach the very complex aromatic oxidation process. But also, data of this type have proved invaluable in determining the accuracy of detailed chemical modelling. Utilizing data on methane oxidation from the turbulent flow reactor, Westbrook at Lawrence Livermore Laboratory in cooperation with Dryer at Princeton has modelled the reaction kinetics over an extended temperature, stoichiometry and pressure (9). Such modelling results provided further insight into the kinetic mechanisms and radical pool responsible for the oxidation processes. In the case of methane oxidation, Westbrook _et al_, have clearly shown that methyl radical reactions procede slowly and as a consequence, methyl radical recombination provides an important route of radical destruction. Thus, ethane (and subsequently ethene) oxidation plays an important role in all but the very leanest oxidation conditions for methane. In addition, modelling has substantiated the importance of hydroperoxy radicals as proposed by Dryer and Glassman (1) as well as delineating the temperature and pressure range over which hydroperoxy can be expected to be important.

The kinetic modelling of the flow reactor results as demonstrated by the Westbrook-Dryer work has a most exciting potential for the study of many hydrocarbon oxidation systems and certainly for our aromatic work as well. Kinetic modelling extends the worth of the flow reactor in its ability to provide data from which elementary rate data may be developed under conditions applicable to real combustion systems.

1. The Turbulent Flow Reactor

Basically, the Princeton flow reactor technique utilizes a heated cylindrical Quartz duct 10 cm in diamter through which a hot inert carrier gas flows at velocities which yield Reynolds numbers in excess of 3500 (Figure 1). The reactor assembly is constructed so that the reactor walls rapidly equilibrate to the local gas temperature. Rapid mixing of small amounts of prevaporized reactant with the carrier is provided by radial injection at the throat of a high velocity mixing inlet nozzle. Proper adjustment of carrier temperature, flow velocity and reactant concentrations result in a steady, one-dimensional, adiabatic reaction zone extending over a length of approimately 85cm. Simultaneous thermal and chemical data at discrete longitudinal locations in the reaction zone are obtained by longitudinal extension of an instrumented probe. Temperature measurements are made with a silica coated Pt/Pt Rh thermocouple, and gas samples are removed through a wtaer cooled/expansion quenched stainless steel sampling probe. Consistent with the long range objective of more complex hydrocarbon oxidation studies, a sophisticated gas chromatographic chemical analysis procedure which was developed in the program permits measurements of all stable hydrocarbon species (including partially oxidized compounds) as well as H_2 and O_2 to 1% precision.

Several unique advantages of this approach should be emphasized. By restricting experiments to highly diluted mixtures of reactants, and extending the reactions over large distances, gradients are such that diffusion may be neglected relative to convective effects; thus the measured specie profiles are a direct result of chemical kinetics only. This is in contrast to low pressure one-dimensional burner studies where diffusion effects must be determined analytically before useful chemical kinetic data are obtained. While this procedure has progressed significantly in its refinement, estimation of diffusive corrections remain very difficult.

Furthermore, in the flow reactor uniform turbulence results not only in rapid mixing of the initial reactants, but radially one-dimensional flow characteristics. Thus "real" time is related to distance through the simple plug flow relations. However, the relation of a specific axial coordinate to real time is not well-defined since the initial time coordinate occurs at some unknown location within the mixing region.

One would suspect that initial mixing history might therefore alter reaction phenomenon occuring downstream. However, the existence of very fast elementary kinetics, which initiate chemical reaction before mixing is complete, permit rapid adjustment of the chemistry to local conditions as the flow approaches radial uniformity. Furthermore, the large dilution of the reactants and rapidity of the kinetics reduce the coupling of turbulence and chemistry to the point that local kinetics are functionally related to the local mean flow properties. This conclusion is experimentally supported by excellent agreement of the derived chemical kinetic data with that obtained from shock tubes and static reactor systems at other temperatures. Agreement also substantiates that the reactor surfaces do not significantly affect the gas phase kinetics. Comparison of flow reactor data from reactor tubes of significantly different surface to volume ratio also corroborates this conclusion. Finally, and most important, the turbulent flow reactor approach permits kinetics measurements in a temperature range (800-1400 K) generally inaccessible to low temperature methods (fast flow Electron Spin Resonance, Kinetic Spectroscopy techniques, static reactors, etc.) and high temperature techniques (shock tubes, low pressure post flame experiments).

The experimental studies are carried out in an arc plasma heated turbulent flow system reactor (Figures 2 & 3). A direct liquid gas conversion system is the source of nitrogen carrier gas. Possible contaminants from anode/cathode erosion in the plasma jet have been controlled through a composite material design derived during the custom construction of the jet (TAFA division of

Humphrey's Corp., Bow, N.H.). Ions are eliminated in a recombination/mixing plenum far upstream of the reactor. Available instantaneous heating characteristics accommodate rapid run preparation and maximum system temperatures to greater than 1400K (the limit is imposed by reactor assembly materials). A ceramically filled, resistance heated inlet section mounted between the arc plasma generator and the reactor assembly has been designed to independently accommodate addition of up to two (thermally stable) reactant species as well as pre-vaporized water. This section is also necessary to produce uniform turbulent flow prior to the reactor assembly. Inlet temperature to the assembly are monitored in this section with thermo-couple instrumentation.

The reactor assembly itself is designed similar to the schematic of Figure 1. The main reactor tube is of fused silica ten centimeters in diameter and approximately 185 cm in length including a 28 cm nozzle inlet mixing section. Fused-silica walls further assure elimination of surface reaction effects. There are two additional reactor tube inserts available to reduce the test section diameter to 7.0 and 5.0 cm. Thus the reactor residence time range can be significantly shortened (factor of 4) and reactor surface-to-volume ratio increased (factor of 2). The reactor mixing inlet can accommodate independently controlled addition of up to 3 reactant species, including a pre-vaporized liquid.

Gas samples are withdrawn through a water-cooled, convective quenched stainless steel probe with quenching gradient of greater than 5×10^6 °K/sec. A Quartz coated Platinum, Platinum-

Rhodium thermocouple with water-cooled jacket is used to measure the longitudinal reactor temperature distribution. Sampling instrumentation is extended longitudinally through the reactor section along its center line.

Gas samples withdrawn at up to twenty discrete longitudinal positions in the reactor are currently stored at low pressure in an all glass/teflon sampling assembly. A new approach which will accommodate heated sampling and storage has been developed. This technique stores small volume samples at near atmospheric pressure in a 16 position heated sample valve. Stable species including CO, CO_2, aldehydes, alkanes, and other carbon containing species will be measured using Hewlett Packard 7624 and 5840 Research Gas Chromatograph Systems equipped with electronic integrators and modified catalyst Flame Ionization detectors (10). This approach permits identical sensitivity per gram atom of carbon for <u>all</u> carbon containing species ($\pm$1% Precision). Hydrogen, oxygen and nitrogen compounds are determined by thermal conductivity ($\pm$3% Precision). In anticipation of work on aromatic oxidation a Hewlett-Packard 5985 Gas Chromatographic/Mass Spectrometric (GC/MS) system has been installed in the laboratory. The addition of mass number and cracking pattern to the GC retention time will allow for rapid identification of product species, particularly the more complex molecules. Early experiments with toluene have verified the need for the GC/MS system.

The reactor assembly will eventually be equipped with optical windows at several longitudinal positions. Thus some integrated spectroscopic measurements, for example, that of [OH] by absorption, will be possible. This approach, when adapted, will be applied most frequently in flow reactor research concerned with elementary kinetic studies.

2. Ethene Pyrolysis

As stated above, the important role of ethene in the oxidation of the paraffins made it important that more be learned about ethene pyrolysis under flow reactor conditions. Ethene pyrolysis studies were completed under the program and presented as part of a paper at the Western States Combustion Institute Meeting in April 1978 (11). The results reported below are abstracted from this paper.

a) Review of Previous Ethene Pyrolysis Work

Gas phase homogeneous decomposition studies of ethylene have been reported by various authors covering the temperature range from 770K to 2300K. The high temperature investigations above 1500K were carried out behind reflected shocks, and time resolved spectroscopy (Roth and Just, Ber Bunsenges, Phys. Chem. 77, 1114 (1973); Homer and Kistiakowsky, J. Chem. Phys., 47, 5290 (1967) or mass spectroscopy (Gay, et.al., J. Phys. Chem., 45, 2371 (1966)) were applied to determine the C_2H_4disappearance and the product formation. C_2H_2 and H_2 were identified as the main reaction products. The pyrolysis is reported to obey a first order rate law in C_2H_4 and the reported activation energies are in good agreement. The authors concur that the overall rate is due to a complex mechanism and deduced the following rate expression from an examination of the pressure dependence of the reaction:

$$-\frac{d[C_2H_4]}{dt} = k_{ov}\ [C_2H_4]^{1.0}\ [M]^x$$

where x represents the dependence of the overall rate constant k_{ov} on the inert gas concentration [M] and was found to range between -0.5 and -0.75.

In the range from 1250 to 1850K the reaction was studied in single-pulse shock tubes (Skinner and Sokoloski, J. Chem. Phys. 64, 1028 (1960); Koslov and Knorre, Kinet. Katal 4, 189 (1963)). The gas chromatographic product analysis again confirms that C_2H_2 and H_2 are the major high temperature products. However, with decreasing temperature the C_2H_2 formation decreases in favor of the formation of butadiene. Activation energies from these studies range from 40 to 50 kcal/mole.

At still lower temperatures, conventional static (Boyd, et. al., Can. J. Chem 46, 2415, 2427 (1968) ; Kunugi, et.al. J and EC Fund. 8, 374 (1968)), and flow systems were used to investigate the pyrolysis. The analysis of experiments with pure C_2H_4, assuming bimolecular disproportionation as the initiation reaction resulted in activation energies of 40 and 49.6 kcal/mole for the overall rate expression.

b) Proposed Mechanisms

Several different approaches have been undertaken in order to explain the kinetic behavior of the C_2H_4 pyrolysis. In general, the reaction is assumed to proceed via a chain mechanism of the Rice-Herzfeld type. However, there is no agreement whether the initiation step is a simple unimolecular C-H bond fission

(R1) or a bimolecular disproportionation (R1a). In addition, the influence of the four-center elimination of hydrogen has to be taken in account at elevated temperatures (R1b)

$$C_2H_4 + M \rightarrow C_2H_3 + H + M \qquad R1$$

$$C_2H_4 + C_2H_4 \rightarrow C_2H_3 + C_2H_5 \qquad R1a$$

$$C_2H_4 + M \rightarrow C_2H_2 + H_2 \qquad R1b$$

In spite of the formation of C_2H_2 and H_2 as the major high temperature decomposition products it is obvious that the overall reaction cannot be explained alone by an α-β elimination (R1b). This kind of reaction has shown to require a considerable amount of energy in excess to the heat of reaction (Benson, Thermochemical Kinetics, Wiley, 1968) due to the complex structure of the involved transition state. The reported activation energies are much too low to account for reaction R1b. At lower temperature Gay et al. determined that the HD appearance in C_2H_4- C_2D_4 pyrolysis experiments is much too fast to be accounted for by the H_2 and D_2 exchange reaction. This indicates that at lower temperatures the influence of reaction R1b is negligible compared to an overall chain mechanism.

Benson and Haugen (J. Phys. Chem 71, 1935 (1967)) had earlier proposed a chain mechanism with reaction R1a as the initial step and compared the predicted reaction behavior with the experimental results of Skinner and Sokoloski. Aside from the ability to predict the observed product distribution the overall activation energy required for the proposed mechanism is significantly higher than the reported values of E_a from the above studies. However, lowering of the temperature and increasing the C_2H_4 concentration will certainly increase the contribution of reaction R1a as initiation of the chain propagation. In a previous study Just and Roth (16th Int'l. Sym. on Comb., p. 761 (1977)) succeeded in measuring the C-H bond fission as an initial step of the C_2H_4 decomposition. They applied atomic resonance absorption spectrophotometry to determine H atoms, and they studied the reaction of 20-800 ppm C_2H_4 in argon mixtures in the range 1700 to 2200K. By comparison with results of additional studies using time resolved infrared spectroscopy to monitor the C_2H_4 disappearance in the early stages of the pyrolysis, Just and Roth (Ber. Bunsenges, Phys. Chem. 77, 114 (1973)) found evidence that C_2H_4 decay was observed after the first stage of the reaction, indicating that the initial reactions very probably are followed by a chain mechanism. Based upon reaction 1 as the initiation step, Roth and Just proposed the following chain mechanism to interpret the observed overall rate of ethylene disappearance and acetylene formation

$$C_2H_4 + M \rightarrow C_2H_3 + H + M \qquad R1$$

$$H + C_2H_4 \rightarrow C_2H_3 + H_2 \qquad R2$$

$$C_2H_3 + M \rightarrow C_2H_2 + H + M \qquad R3$$

$$H + C_2H_3 \rightarrow C_2H_2 + H_2 \qquad R4$$

$$H + C_2H_3 + M \rightarrow C_2H_4 + M \qquad R5$$

This mechanism includes initiation (R1), propagation (R2, R3) and termination (R4, R5), neglecting the termination reactions

$$2C_2H_3 + M \rightarrow C_4H_6 + M \qquad R6$$

$$H + H + M \rightarrow H_2 + M \qquad R7$$

A steady state treatment of the radicals H and C_2H_3 allows for an estimate of the overall activation energy based upon the activation energies of the individual reactions. A value of $E_a \approx 58$ kcal/mole is in good agreement with the experimental results. Furthermore the proposed mechanism predicts the observed pressure dependence within reasonable limits.

c) Current Results

In agreement with the cited high temperature studies of the ethylene pyrolysis the product analysis of the present flow reactor experiments shows acetylene and hydrogen as the major reaction products. Butadiene was the only detectable minor product and was found only in small concentrations. Results of a pyrolysis run at 1220K are represented in Fig. 4 in the form of a plot of species concentration and temperature versus the position in the reactor duct (which is proportional to the reaction time). The ethylene concentration decreases with increasing reaction time and, simultaneously, hydrogen, acetylene and butadiene , are formed. Due to the endothermicity of the reaction the temperature drops about 10 degrees K. The total carbon concentration calculated from all carbon containing species is constant over the observation time of the experiment thus assuring that no other major intermediate products are present. Within the error limits of the measurements, the rates of hydrogen and acetylene formation are equal. Neglecting the formation of butadiene, the rate of ethylene disappearance and the rates of hydrogen and acetylene formation can be described by

$$- \frac{d[C_2H_4]}{dt} = \frac{d[C_2H_2]}{dt} = \frac{d[H_2]}{dt} = k_{ov}\ [C_2H_4]\ . \qquad (1)$$

Rate constants, k_{ov}, have been determined from the slope of plots for ln $[C_2H_4]$ versus time as well as from the rates of H_2 and C_2H_2 formation.

Values of k_{ov} thus obtained are plotted in Fig. 5 and show good agreement with the results of the previously stated investigations. A pressure dependence of $k_{ov}\ [M]^{-0.6}$ was chosen to represent all data. This is in close agreement with the observed pressure dependence of earlier work, where the inert gas pressure has been varied (Roth and Just, Ber. Bunsenges, Phys. Chem. 77, 1114 (1973), Gay et.al, J. Chem. Phys. 45, 2371 (1966)). No corrections have been applied to account for the collision efficiency of the various collision partners. Because the collision efficiency of C_2H_4 is significantly greater than that of N_2 or Ar, a lowering of k_{ov} by a factor of 2 to 3 is required for a comparison with the low temperature pure C_2H_4 study (Kunugi, et. al, J. and EC Fundaments 8, 374 (1969)).

All values of $k_{ov}\ [M]^{-0.6}$ represent rate constants for the ethylene depletion accordingto an overall mechanism. Results of Skinner and Sokoloski (J. Phys. Chem. 64, 1028 (1960)) that originally reported the conversion of C_2H_4 to C_2H_2 and to C_4H_6 as distinct terms have been accounted for in this comparison.

With regard to the different reaction systems and analysis methods which have been used to examine the C_2H_4 pyrolysis, both temperature dependence as well as the absolute values of k_{ov} are in good agreement over an extended temperature range. From a correlation of the data of Fig. 5, we recommend an activation energy of 56.3 kcal/mole for the ethylene overall decomposition. Assuming that the term $[M]^{-0.6}$ represents the valid pressure dependence of the reaction, the Arrhenius equation is given by

$$k_{ov} = 7.0 \cdot 10^{-2} \exp(-56.3/RT)\,[\mathrm{cm}^3/\mathrm{molecule}]^{-0.6}\,\mathrm{sec}^{-1}.$$

Further investigations will examine if the observed pressure dependence can be extended to the low temperature region.

d) Discussion

At high temperatures and low initial C_2H_4 concentrations the mechanism (R1-R5) proposed from Roth and Just adequately explains the available data on ethylene pyrolysis. A steady state treatment of the H and C_2H_3 radical concentrations for Reactions R1 to R5 yields the rate equation:

$$-\frac{d[C_2H_4]}{dt} = \frac{d[H_2]}{dt} = \frac{d[C_2H_2]}{dt} = k_3[C_2H_3] + k_4[H][C_2H_3] \; . \qquad (2)$$

This equation requires that the rate of C_2H_4 decay is equal to the rates of H_2 or C_2H_2 formation, which is in agreement with the results of this study.

However, the same mechanism cannot be valid over the entire temperature range. The question is how to extend this mechanism and whether the extended mechanism can explain the change in product formation, which has been observed as a function of temperature, ethylene concentration and total pressure. In order to explain the formation of butadiene at lower temperature and at higher C_2H_4 concentration reaction 8

$$C_2H_3 + C_2H_4 \rightarrow C_4H_6 + H \qquad R8$$

as an alternative chain propagating reaction has to be taken into account. With decreasing temperature the unimolecular decomposition of C_2H_3 (R3) will be suppressed in favor of reaction R8. In addition, an increase in the C_2H_4 concentration results in an increase in the rate of butadiene formation. Skinner and Sokoloski performed experiments with 0.5% C_2H_4 in argon and observed C_2H_2 as a major and C_4H_6 as a minor product. At the same temperature the $C_2H_2 : C_4H_6$ ratio was found to be inverted at ethylene concentrations of 6% in argon.

Experiments with pure C_2H_4 at still lower temperatures exhibit such a variety of products that obviously the proposed mechanisms (R1-8) has to be extended to include a larger number of bimolecular reactions.

3. Rich Oxidation Studies of Ethene

The oxidation of ethene has been studied under fuel rich conditions for the temperature range 950 to 1110K in the flow reactor. A fuel equivalent range of $1 < \phi < 11$ has been studied in which the minimum oxygen concentration corresponded to 0.7%.

Cursory observation shows that experiments with C_2H_4 - O_2 mixtures exhibit a significant change in the product distribution compared to the product distribution of the pure pyrolysis. A broad spectra of stable intermediates together with final oxidation products is observed.

In general the same products are observed in all the experiments, although there is a change of the relative product distribution depending mainly on the total oxygen concentration.

A representative analysis of a fuel rich run is shown in Fig. 6.

CO, H_2O, and H_2 appear as main reaction products and CH_4, CO_2, C_2H_2, C_2H_6, HCHO, CH_3OH, C_2H_8, and CH_3CHO represent minor products. Concentrations of C_3H_8 and CH_3CHO are found to be smaller than that of C_2H_2 and are not plotted in Fig. 6. Both major and minor products increase continuously with corresponding decrease of fuel and oxidizes concentration except HCHO which attains a maximum in its concentration versus distance curve. Due to the relatively small oxygen concentration the rate of C_2H_4 disappearance is small and the total conversion does not exceed about 70% within the observation time in the fuel rich experiments.

In addition the heat release of the overall process is slow due to the fact that CO oxidation to CO_2, which is the main exothermic reaction step, is still negligibly small. A comparison of experiments with different oxygen concentrations under otherwise constant reaction conditions indicate that the rate of C_2H_4 conversion has a significant dependence on oxygen. In contrast the product distribution is affected very little by the variation of the oxygen concentration. However, with decreasing equivalence ratio the rate of intermediate oxidation overtakes the rate of formation so that all the minor species concentrations attain a maximum within the observation time of an experiment.

In order to represent the oxidation process in terms of an overall expression a correlation of the rate data in the form of

$$\frac{-d[C_2H_4]}{dt} = A \exp\left(-E_{ov}/RT\right) [C_2H_4]^a [O_2]^b$$

was derived. The parameters A, E, a and b were determined experimentally with the aid of least squares fitting techniques. Figure 7 shows the results of the fuel rich experiments. The line represents the least squares fit of the data and yields the expression

$$-\frac{d[C_2H_4]}{dt} = 10^{20.3} \exp\left(50{,}300+3000/RT\right) [C_2H_4]^{0.8} [O_2]^{1.5}$$

$$1 < \phi < 11 \qquad\qquad 950\ K < T < 1110\ K$$

This expression has to be understood as the empirical description of the C_2H_4 depletion within the stated temperature and equivalence ratio limits at atmospheric pressure. The representation of data in terms of Arrhenius parameters was found to be useful but does not allow comparison to Arrhenius parameters of elementary reactions.

4. The Pyrolysis of Propane

A study of propane pyrolysis has been undertaken to elucidate the important fuel-radical reactions dominant in the pyrolysis process. Of special interest is the role of the propyl radical since propane is the first alkane which possesses radicals with chemical isomers (normal and isopropyl).

Propane pyrolysis studies have recently been reviewed by Volkan and April (Ind. Eng. Chem., Process Des. Dev., 16, 429 (1977)) and will not be repeated here. Although the general features of the pyrolysis mechanism are agreed upon, detailed understanding is still lacking. The need for further detailed product measurement over the important intermediate temperature range of 1100 to 1300K of the quality required for kinetic modelling further encouraged application of the turbulent flow reactor to the propane problem.

A series of pyrolysis experiments for the temperature range of 1120 to 1240K have been conducted over a propane concentration range of 1.2×10^{-8} to 1.2×10^{-7} moles/cc (the balance of the flow was nitrogen). Although the data of the present experiments are still under consideration, several intermediate results can be presented. Figure 8 shows the reactant-product distribution for a single pyrolysis experiment using the flow reactor. Consistent with previous investigators, the major products observed are ethene, propene, methane and hydrogen with smaller amounts of ethane, acetylene and butadiene. Analysis of the pyrolysis results have proceeded from two independent approaches: an overall rate approach and a detailed kinetic model approach.

In the overall rate approach the propane di[illegible]ance rate is represented as

$$-\frac{d[C_3H_8]}{dt} = 10^A \exp -E_{ov}/RT\ [C_3H_8]^n \qquad (3)$$

where A, the pre-expontial factor, E_{ov}, the activation energy, and n, the reaction order are determined from the data. The order of the reaction can be found by plotting the log of the rate verses the log of the concentration of propane with the slope of this plot yielding n. Analysis of the flow reactor experiments indicate that the reaction order varies as the reaction proceeds. Initially the order starts at 1 and increases to as much as 1.7. This is of particular interest since past studies determine the order to be between 1 and 1.5. Thus the discrepancies in past work could be related to differences in the extent of reaction observed. Support for such a conclusion has been reported previously (Buekens and Froment I&EC Process, Des. Dev. 7, 435 (1968)), but not over such a wide range of operating conditions as in the present study.

To shed further light on the importance of the extent of the reaction, a plot of the ratio of the mass of product and extent of reaction was plotted verses the extent of reaction (see Fig. 9). In this plot the extent of reaction is given as $([C_3H_8]_o - [C_3H_8])$ where $[C_3H_8]_o$ is the initial propane concentration and all concentrations are in gm/cc. The striking point of this plot is that all of the products are characterized by a nearly constant ratio throughout the reaction. Thus the amount of product produced per unit extent is a constant versus extent of reaction. This would point to a steady state situation in which the radical pool is relatively constant throughout the reaction.

As a comparison with other workers, the pyrolysis data has been analyzed as a first order rate law and compared with past studies. As can be seen in Figure 10 the results compare quite well with previous workers over a wide temperature range. This lends further support for the applicability of the flow reactor technique to obtain kinetic results.

In order to obtain a more detailed representation of the pyrolysis mechanism a kinetic modelling approach is being applied to the present results. A thirty-one step mechanism shown in Table 1 is being used to model the pyrolysis results. Numerical integration techniques are being used to predict the rates of disappearance and production of reactants and products. Attention is being given to the reactions producing and involving propyl radicals (20).

The results of the detailed kinetic studies will be used to provide better insight into the overall rate described above. In addition, the improved understanding of propyl radical reactions will be of great value to the rich oxidation studies which are to follow.

C. Pyrolysis and Oxidation of Aromatics

1. Review and Some New Analysis (16)

Studies of the oxidation of aromatic hydrocarbons have sporadically occurred over the last fifty years. The earliest studies [Fort and Hinselwood, Proc. Roy. Soc. A 127, 218 (1930); Amiel, Am. Chem. 7, 70 (1937)] were concerned with the oxidation of benzene and established the chain branching nature of the aromatic oxidation process. Other workers [Norrish and Taylor, Proc. Roy. Soc. A 234, 160 (1956); Newett and Burgoyne, Proc. Roy. Soc. 171, 421 (1939); Burgoyne, et al., Proc. Roy. Soc. 174, 379 (1940); Burgoyne, Proc. Roy. Soc. 174, 394 (1940); Donald and Grover, Spec. Supp. Chem. Eng. Sci. 3, 31 (1954); Norrish and Taylor, Proc. Roy. Soc. 238, 143 (1956)] extended the range of pressure and temperature and considered the oxidation of the alkyl substituted benzenes. These studies were generally carried out in static reactor systems at low temperature (600°C) and determined only the major and minor oxidation products. From the product distribution, kinetic mechanisms could be postulated using thermodynamic arguments, but the determination of specific kinetic rates were not possible.

In general, the oxidation of aromatics can be viewed to have the following sequence of reactions:

1) initiation
2) aromatic ring fragmentation
3) chain branching
4) production of the major oxidation products: CO, CO_2, and H_2O.

It appears the specific characteristics of steps (2) and (3) (the ring fragmentation and chain branching reactions) may differ substantially for different aromatic compounds. These differences may have significant effects on the production of soot; this subject will be touched on later in this section.

The initiation reaction for the oxidation of aromatic hydrocarbons at low temperatures is postulated to occur through hydrogen abstraction by molecular oxygen. Thus, for benzene one may write

$$C_6H_6 + O_2 \rightarrow C_6H_5 + HO_2 \qquad \text{(R9)}$$

This step is followed by the formation of a peroxide compound which in the case of benzene is

$$C_6H_5 + O_2 = C_6H_5OO \qquad \text{(R10)}$$

This initiation sequence is thought to apply to the alkyl substantiated aromatics in an analogous manner. In analogy to the oxidation of alkyl radicals at higher temperature, the reverse of Reaction R10 dominates.

The evidence indicates that no one single mechanism can account for the product distribution observed for the oxidation of different aromatic compounds. In the case of benzene, the high phenol yield [Norrish and Taylor, Proc. Roy. Soc. A 234, 160 (1956)] suggests that ring fragmentation may be due to hydroxyl addition to the benzene ring via

$$C_6H_5OO + C_6H_6 \rightarrow C_6H_5O + C_6H_5 + OH \qquad (R11)$$

$$C_6H_5O + C_6H_6 \rightarrow C_6H_5OH + C_6H_5 \qquad (R12)$$

$$C_6H_5OH + O_2 \rightarrow C_6H_4(OH) + HO_2 \qquad (R13)$$

$$C_6H_4(OH) + O_2 \rightarrow C_6H_4(OH)OO \qquad (R14)$$

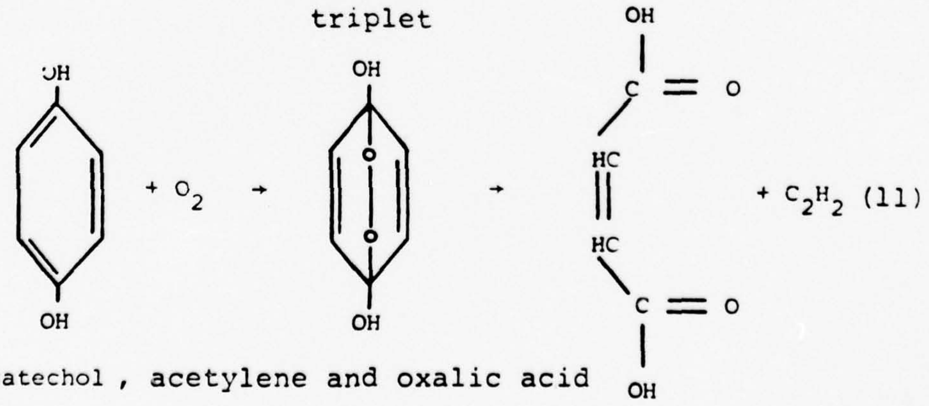
$$C_6H_4(OH)OO + C_6H_6 \rightarrow C_6H_5O + C_6H_4(OH)_2 \qquad (R15a)$$

$$\rightarrow C_6H_4(OH)O + C_6H_5(OH) \qquad (R15b)$$

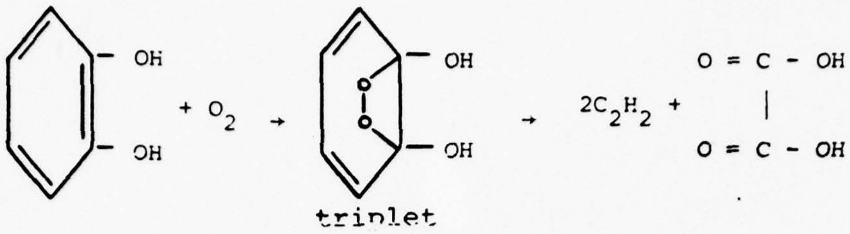
$$C_6H_4(OH)O + C_6H_6 \rightarrow C_6H_4(OH)_2 + C_6H_5 \qquad (R16)$$

Reactions 15a and R15b are obviously overall steps since as written they are not sterically feasible.

The detection of both pyrocatechol and hydroquinone as minor products in the oxiation of benzene give some support for this mechanism. These dihydroxy benzenes are unstable with respect to oxidation and it has been suggested that they react with oxygen in the following manner to form actetylene and maleic acid from hydroquinone.



and for pyrocatechol, acetylene and oxalic acid



(12)

However, the intermediate compounds are triplets and thus the first step in the above reactions are "spin resistant" and may not proceed. Further, even if they did, the decomposition step back to hydroquinone and pyrotechol would be favored, particularly at high temperatures. Nevertheless, as described later, some compounds such as maleic and oxalic acids must form. The oxidation of acetylene follows, accompanied by chain branching and significant heat release. The production of acetylene in this reaction is noteworthy since it is thought to be along with benzyl radicals, a precursor of soot formation [Tesner, et al., Comb. and Flame 17, 279 (1971); Tesner, et al., Comb. and Flame 17, 253 (1971)]. The successive addition of unsaturated hydrocarbons to aromatic free radicals can eventually lead to the formation of larger condensed-ring compounds. Acetylene addition offers a likely path for the formation of large free radicals since such radicals should be stable with respect to reverse reaction.

Even given these uncertainties there is some high temperature results which support a mechanism of the type described. Fujii and Asaba (14th Int'l. Comb. Sym. (1973) p. 433) have observed both biphenyl and acetylene production in rich oxidation of benzene in the temperature range of 1300 to 1700K using a single-pulse shock tube technique, and propose reactions which involve the phenyl radical or acetylene as the precursors to soot formation. In addition, the authors argue that the CO production they observed can only be explained through a peroxide intermediate as in Reaction R10.

For the case of alkyl substantiated benzenes, reactions involving the alkyl substitute as opposed to the ring itself must be taken into account. Studies indicate that these side ring reactions predominate at low temperature while ring rupture becomes more important at higher temperatures. In addition, studies of the oxidation of the xylenes [Bernard and Sankey, Comb. and Flame 12, 353, 345 (1968); Wright, J. Phys. Chem. 66, 2023 (1962), 64, 1944 (1960)] have shown that the ortho-xylene the ring fragmenting step is not due to the oxidation of a dihydroxy benzene species, since neither pyrocatechol nor hydroquinone have been detected. Oxygen attack of the ring regardless of what alkyl substitute is present seems more likely from the product distributions for the oxidation of o-xylene. Thus the detailed mechanisms for oxidation of benzene and xylene show a marked difference.

The impact of such differences on the combustion products of aromatic fuels could be dramatic. As previously pointed out the production of acetylene is an important precursor to the formation of soot [Tesner, et al., Comb. and Flame 17, 279, (1971); Tesner, et al., Comb. and Flame 17, 253 (1971)], changes isomer has a maximum reaction rate which is ten times that observed for the meta and para isomers. This observation is not entirely surprising since early studies of aromatic compounds as fuels determined the critical compression ratios for ortho, meta and para-xylene to be 9.6, 13.6, and 14.2 respectively.

Attempts to explain this marked difference in reaction rate have concentrated on the occurrence of a reactive intermediate such as o-tolualdehyde [Wright, J.Phys.Chem. **66**, 2023(1962)] or o-xylene oxide [Loftus and Saterfield, J.Phys.Chem. **69**, 909 (1965); Barnard and Sankey, Comb. and Flame **12**, 353, 345 (1968)]. In each case intramolecular isomerization steps are considered to be important. It also appears that the ring fragmenting step is not due to the oxidation of a dihydroxy benzene species, since neither pyrocatechol nor hydroquinone have been detected. Oxygen attack of the ring regardless of what alkyl substitute is present seems more likely from the product distributions for the oxidation of o-xylene. Thus the detailed mechanisms for oxidation of benzene and xylene show a marked difference.

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To date, studies of the oxidation of aromatics have been limited to low temperatures ($T < 650$°C) and, thus, the extrapolation of the mechanisms discussed above to higher temperatures is very uncertain. Indeed, some of the compounds mentioned above may not be present at higher temperatures. Results of the low temperature work dramatically point to the need for the more detailed studies at the higher temperatures that we have undertaken. For example, Loftus and Satterfield [J. Chem. Phys. **69**, 909 (1965)] in their study of o-xylene oxidation observed that as the temperature is raised the percentage of conversion of o-xylene to product due to ring rupture rises dramatically. At 455°C compounds formed through ring rupture accounted for only 17% of the reacted o-xylene while at 510°C the value was 46%. A similar study of the oxidation of xylene by Wright [J. Chem. Phys. 66, 2023 (1962)] showed that approximately 66% of the reacted xylene underwent ring rupture at 650° C. It is clear therefore, that as the temperature is raised further ring fragmentation processes should play an even more dominant role. Indeed, it is in this higher temperature region that typical combustion processes occur.

An additional interesting point has been made by Wright [J. Chem. Phys. 66, 2023 (1962)] concerning the CO/CO_2 ratio. Skirrow and Tipper [7th Comb. Symp., Butterworth's, London, p. 134 (1958)] have observed from a survey of a number of gas phase oxidations of paraffins, olefins, and aldehydes that the CO/CO_2 ratio for fixed temperature decreases as the oxygen/fuel ratio is increased and increases with increasing temperature for fixed composition. The low temperature oxidation studies of aromatics show the opposite effect to be true [J. Chem. Phys. 66, 2023 (1962)]. Thus it appears that the mechanisms for production of CO and CO_2 from oxidation of aromatic compounds differs from that for aliphatics.

It is our opinion that these results offer a clue to the mechanism for the production of CO and CO_2 in the oxidation of armoatics. It is known that in alkyl oxidation CO is formed via the formyl (HCO) radical and is then oxidized to CO_2 predominately by the hydroxyl radical

$$CO + OH \rightarrow CO_2 + H \qquad \text{(R19)}$$

Thus the observed trends of the CO/CO_2 ratio for aliphatic oxidation can be explained by the effect of the initial oxygen concentration in hydroxyl concentration. The explanation of the temperature effects is more complex and not entirely clear.

Although there are not CO/CO_2 data on benzene oxidation, Reactions R17 and R18 show that CO can form through two routes: (1) directly from carboxyl radicals (0 = C - OH) formed, and (2) from oxidation of the formed aliphatic compounds which lead to CO_2 via CO. The fact that Wright observes an increasing CO/CO_2 ratio with increasing oxygen/fuel ratio indicates that compounds containing carboxyl groups form prior to the oxidation of any aliphatic group present. Wright's experiments, like most of the early aromatic work, were performed very fuel rich. Thus, initially, all the CO_2 formed from the attack on carboxyl radicals. As the oxygen concentration was increased, the aliphatics were oxidized to give CO. Indeed, if the experimental mixture ratios were closer to stoichiometric the same trends as that observed with the aliphatics should prevail.

Two arguments can be offered to support the contention that CO_2 forms directly from the carboxyl radical. First, it has been established that the step occurs in solution chemistry (Cram and Hammond, Organic Chemistry, McGraw-Hill, p. 472). And, second, it is not likely that the C-O bond in the carboxyl radical would break thermally at the low experimental temperature used because the radical is stabilized by large molecular resonance.

How the maleic and oxalic acids form in benzene oxidation must still be considered uncertain. Even further it would appear difficult to break off a carboxyl group in maleic acid.

The CO/CO_2 ratios found suggest, however, that even though hydroquinone and pyrotechol have not been formed in the oxidation of the alkylated benzenes, some carboxyl structure must develop in an intermediate formed during this oxidation.

Irrespective of being able to detail the proper mechanisms, it does appear that production of CO and CO_2 from the oxidation of aromatic compounds differs from that for aliphatics at least at low temperatures. This difference could also explain why aromatics soot more readily in diffusion flames.

2. Experimental Program and Results

The intent of the current program is to elucidate the oxidative mechanisms of some aromatic fuels with a particular emphasis on those mechanisms which lead to soot and other pollutant formations, since insights already have been obtained as outlined in the previous sub-section. The major emphasis was to obtain experimental results in the Princeton flow reactor. With the realization that complex intermediates would most likely play a key role in the understanding of aromatic oxidation, it was proposed that during this grant year that instrumentation and chemical analysis techniques would be developed and that initial experiments for obtaining qualitative comparison of oxidation reactions for various elementary aromatic compounds would be performed. Specific emphasis was placed on observing production and reaction of acetylene. These objectives have been met with greater success than anticipated.

During the grant year we have been able to purchase and develop into a fully opeartional mode a Hewlett-Packard Gas Chromatographic/ Mass Spectrographic System. Further, a new heated sampling system has been designed and ordered.

While these developments were taking place, our initial oxidation tests with aromatics were begun. Unfortunately OSHA restrictions prevented us from using benzene until our laboratory can be determined to meet the proper standards for handling benzene.

Nevertheless, we have been able to continue our qualitative studies using toluene. Since no aromatic oxidation experiments had previously been performed with the flow reactor, and there was a concern about the production of heavy intermediates, it was decided to operate initially with lean mixtures. The hope was that such an operation could prevent a large accumulation of such intermediates which might be lost through condensation before being collected in the sample bottles. Figure 11 shows the flow reactor results for the lean oxidation of toluene. A number of interesting observations can be made from these results. Probably most striking is the poor carbon balance as reflected in the CTOT curve. This implies that product species of the reaction are being lost in the sampling/analysis procedure. Approaches addressing this aspect of the aromatic oxidation studies will be given later in this section. One should note that the toluene concentration has been multiplied by a factor of seven in plot shown in Figure 11 for convenience of scale.

Consideration of other aspects of these results leads to two additional observations. First the CO and CO_2 production regions are seen to be essentially sequential in nature. This is similar to previous observations made in this laboratory concerning the oxidation of alkane species (3). This sequential aspect of the oxidation process has been attributed (16) to the competition being OH radical attack of the fuel

$$F + OH \rightarrow F + H_2O$$

and carbon monoxide:

$$CO + OH \rightarrow CO_2 + H.$$

Secondly, the production of acetylene (C_2H_2) in this run is noteworthy. Since in previous alkane studies acetylene was not observed until the equivalence ratio was greater than one. Figure 6 shows the results for a rich ethene run. It is interesting to note that less acetylene is observed in the rich example for ethene ($\phi=1.8$) versus the lean toluene experiment ($\phi=0.05$). It should also be mentioned that the carbon atom concentration for the two experiments are within about a factor of two with the ethene experiment having the higher concentration. Thus the observed acetylene production cannot be attributed to a carbon concentration effect. One must then conclude the toluene is a copious acetylenic producer. This, of course, is fundamental to any mechanism which involves acetylene as a building block to soot formation.

Recent efforts have addressed the previously mentioned carbon balance discrepancies observed. The major processes responsible for the loss of carbon species include:

(1) condensation on the probe
(2) condensation on the sample storage vessel
(3) retention on the gas chromatographic column
(4) lack of detector sensitivity to the product species

The first two processes are presently being addressed by constructing a new sampling system. The column and detector aspects have been approached as analysis technique problems with two approaches being pursued.

The first involve multiple column gas chromatography using our new HP 5840 gas chromatograph. In this technique up to three separate columns are used in a single analysis. The columns are chosen to optimize the separation of particular products. For example, the present columns employ a column optimized for aromatic compounds, one for light hydrocarbons and one for CO, H_2, O_2. These columns are switched in and out of the gas analysis stream under instrument microprocesser control. Application of this approach has shown substantial improvement in the carbon balance curve as can be seen in Figure 12. It should be pointed out that in this figure acetylene and ethene are reported as a single peak since the light hydrocarbon column presently in use does not separate these gases. For comparison one may refer to Figure 11 where one sees the acetylene and ethene are produced in approximately equal amounts. Thus about one half of the ethene observed in Figure 12 is acetylene.

The second approach being taken to address the analysis problem involves gas chromatography/mass spectrometry. The addition of the mass spectrometer offers a nearly universal detector which also provides fast detector response time. This later capability allows for the use of capillary column techniques which provide wide analysis capabilities for gas analysis. Presently the GC/MS is being applied to provide this capability.

D. Soot Formation and Destruction

1. Review and Analysis

Results of much needed studies to explain the fundamental kinetics of soot formation have been reported [Palmer and Cullis, "Chemistry and Physics of Carbon, Vol. I", P.L. Walker, Ed., Dekker, N.Y. Chap. 5 (1965); Lawton and Weinberg, "Electrical Aspects of Combustion", Oxford, Cahp. 7 (1968); Homann and Wagner, 11th Comb. Symp. Combustion Institute, Pittsburgh, p. 271 (1967); Feugier, 2nd International Symp. on Chem. React. Dyn., University of Padua (1975)]. However, there has been little effort to employ this understanding in reducing soot emissions of various practical combustion systems. As one of the major aspects of this program, an extensive review elaborating upon what is known about the formation of soot in flames from a fundamental point of view is being compiled. This review will address the major experimental observations with respect to the physical and chemical variables, how the present accumulated knowledge reflects upon processes occuring in engines and how water, in particular, affects soot formation. Of course, fuel type will be important to these considerations. Although principal concern would be the homogeneous formation of soot in the gas phase, the question of coking of the liquid fuel will be addressed as well.

Another major aspect of the program is to study the role water may play in reducing soot formation in combustion processes. One member of our group has recently reviewed the uses of water as an adjunct to combustion in internal and external systems (12).

This review supports the necessity for this further study. Particularly there appears to be confusion (13) as to the effect of water on soot formation kinetics.

Unfortunately, much of the experimental work with respect to soot formation in practical devices has not been carried out in a fundamental manner. A theory that appears to be a good starting point for understanding of the phenomena in more complex systems suggests that the amount of soot formed depends upon the rate of formation of the precursors (through extensive polymerization-addition reactions that lead to soot nuclei) and the rate of attack on these precursors by oxidizing species such as hydroxyl radicals.

Two experimental approaches were proposed to check this hypothesis. The first is a fundamental approach using the turbulent flow reactor to characterize what could occur in premixed flames. That soot precursors could form even in premixed aliphatic fuel-oxygen system had already been established in the program - and is shown in Figure 13. The work reported earlier on ethene pyrolysis and preliminary oxidation studies also show the formation of acetylene. Thus, it has been shown that acetylene can form in a homogenous premixed-oxidation system. Acetylene and/or radicals produced from acetylene are some of the essential precursors to soot formation. Because of these observations, it was proposed to perform fuel rich ethene oxidation experiments in the turbulent flow reactor with water added. The specific role of water and particularly OH radicals was the goal of these studies.

The second approach was more pragmatic and undertook to measure the relative sooting characteristics of a fuel in a laminar fuel jet diffusively burning in air (Palmer and Cullis, op. cit.). The flow rate of the vaporized fuel could be varied until sooting is observed. The height of the sooting point above the fuel point would be a measure of sooting characteristic of the fuel. The larger the height, the less the tendency to soot. Although numerous results obtained in this manner have been reported, there appear to be none in which water vapor (or other materials) was added to the fuel stream.

2. Experimental Results

Extensive experimentation has been performed during the current contract year. Unfortunately, the tests with respect to water addition are inconclusive and require further study. In the turbulent flow reactor kinetic studies, fuel-rich ethene runs were carried out with and without water addition and the extent of acetylene formation followed. Contrary to our expectations the water addition runs showed greater acetylene formation. Why these results differ from the flame studies of Muller-Dethlefs and Schlader remains to be explained.

It was decided to perform two types of fuel jet studies: One using a liquid pool and another a vaporized fuel jet. The liquid pool experimentation is that given by Clarke et.al. (J. Inst. Petrol., 32, 313 (1946)). The concept appeared simple and conducive to rapid construction. Indeed, experiments were begun in November of 1977. The principle is to vary the width of a liquid pool by raising the level in a funnel shaped container. The qualitative measure of sooting is the so-called sooting height. When the liquid pool is ignited a luminous diffusion flame forms. As the pool level is raised, increasing the pool width, the flame height increases. At a given height, a soot stream breaks through the tip of the flame. This point is the sooting height. The smaller the height the greater the tendancy to soot.

The published approaches required a great deal of development before the experiment could be considered a good reproducible test.

Flame heights were measured for various fuels. The same fuels were emulsified with water and the tests repeated. Unfortunately the emulsified fuel broke down and the effect of the water could not be determined. Steam was added inside the fuel rich side of the flame as well. Although an effect was noticed, a similar effect was obtained when nitrogen gas was added. It was concluded that the liquid pool test was not appropriate for checking the effect of additives on soot reductions. Details of the experimental apparatus and the testing done are reported in Lt. van Treuren's thesis (17).

The apparatus is however ideally suited for the comparative evaluation of the sooting qualities of various fuels. One particularly interesting result involves the study of mixtures of fuels. Figure 14 shows the results fuel mixtures continaing heptane/hexane heptane/hexene and heptane/toluene. These experiments clearly show a different sooting behavior for fuel mixtures continaing an aromatic component. As can be seen relatively small percentages of toluene (15-20%) result in dramatic increases in soot formation as represented by the smoke point as compared to the mixtures containing alkanes and alkenes (18).

Comparative studies of shale and coal derived fuels with conventional JP-4 and JP-5 has also been conducted using fuels obtained from the Aeropropulsion Laboratory of Wright-Patterson AFB. These studies have similarly supported the finding that aromatic content has a critical effect of soot point characteristics. These and other results are further reported in Lt. van Treuren's thesis (17).

In summary, the results of this study confirm the validity of the smoke point test as a parameter to describe the sooting tendency of liquid fuels or fuel blends. When determined under controlled conditions, the smoke point represents a meaningful measure of the ability of a fuel to form soot. Studies with blended fuels show that the sooting behavior of a system is dominated by aromatics over aliphatics. This is an important realization, when considering refining techniques. Even a strong reduction of the aromatic compounds in a fuel mixture does not necessarily result in an equal change of soot formation character, however, a small addition of aromatics to a pure aliphatic system can cause a drastic increase of soot and coke production in the burning process. The detailed, quantitative understanding of this behavior could effect the refining costs for fuel blends.

Since the major objective of the experimental program is to evaluate the effect of water and other additives, the necessity of experimentation with vaporized fuel jets became obvious. A fuel jet apparatus has been designed and constructed. Experimentation has begun and will continue. Studies to date have involved a number of fuels (C_2H_4, C_3H_8, C_4H_{10}, and C_2H_2) and additives (N_2, H_e, Ar, H_20, SO_2 and N_20). The conclusions drawn from these studies indicate that for those additives which reduce sooting the mechanism appears to be thermophysical. More specifically, the results are consistent with a mechanism in which higher heat capacity and lower thermal conductivity and diffusivity favor soot suppression (19).

E. Carbon Oxidation

For large carbon particles burning at high temperatures [Mulcahy and Smith, Rev. Pure Appl. Chem. 19, 18 (1969)] the rate is diffusion controlled. A general burning rate expression for condensed phase fuels is (14).

$$G_f = (\mu/\delta) \ln (1 + B)$$

where G_f is the mass burning rate (gm/sec cm^2), μ is the viscosity of gaseous fluid, and B the transfer number. When the flame is moved to the burning surface; that is, there is surface combustion, but diffusion controlled, B takes on a very simple form (Glassman, op. cit.)

$$B = i\, m_{o_{2,\infty}}$$

where i is the mass stoichiometric index for the oxidation process and $m_{o_{2,\infty}}$ is the oxygen mass fraction in the free stream.

For heterogeneous burning, B is generally small compared to 1, thus

$$\ln (1 + B) \approx B$$

and the burning rate expression becomes simply

$$G_f = (\mu/\delta)\, i\, m_{o_{2,\infty}}$$

Thus, the burning rate is directly proportional to i.

For the reaction

$$C + O_2 \rightarrow CO_2$$

i = 12/16 = 0.750. Consequently if the carbon at the surface is converted only to CO, the burning rate is twice as fast as if it were converted to CO_2. The ramifications of this simple observation can have important practical consequences.

The most oft-quoted model of carbon oxidation is that due to Coffin and Brokaw [NACA TN 3929 (1956)]. They stated that CO is formed at the surface, diffuses away and is oxidized to CO_2 by oxygen which diffuses toward a gas phase reaction zone. The CO_2 formed diffuses back to the surface and oxidizes the carbon via the Boudouard reaction:

$$C + CO_2 \rightarrow 2\,CO$$

If this model were true, then i can be shown to be 12/16.

Unfortunately, many investigators have interpreted Coffins and Brokaw's model as one based on experiment. It has never been experimentally verified. Whether CO or CO_2 forms can be a function of the temperature and composition of the surface. Thus, it was proposed to consider the design of an experiment to measure the gas composition near a oxidizing carbon surface as a function of surface temperature. No firm design has been agreed upon to this point as the approaches of others in the general consideration of carbon oxidation is still being reviewed. That the particular process is temperature dependent is shown in Figure 15, which is a general review of the experimental literature.

References of Work on Program Investigators

1. "Combustion Chemistry of Chain Hydrocarbons" by F. L. Dryer and I. Glassman, Princeton University AMS Report No. 1350, (1977); to appear in AIAA Progress Series.

2. "High Temperature Oxidation of Carbon Monoxide and Methane in a Turbulent Flow Reactor" by F. L. Dryer, Princeton University Ph.D. Thesis Report No. 1034 T (1972).

3. "The High Temperature Oxidation and Pyrolysis of Ethane" by R. Cohen, Princeton University AMS Department Ph.D. Thesis Report No. 1338 T (1977).

4. "The High Temperature Pyrolysis and Oxidation of Acetaldehyde" by M. B. Colket III, Princeton University AMS Department Ph.D. Thesis Report No. 1270 (1975).

5. "High Temperature Pyrolysis of Acetaldehyde" by M. D. Col et III, D.W. Naegeli, and I. Glassman, Int'l. J. of Chem. Kinetics 7, 223 (1975).

6. "High Temperatures Oxidation of Acetaldehyde" by M. B. Colket III, D. W. Naegeli, and I. Glassman, 16th Synp. (Int'l.) on Combustion, Combustion Institute, Pittsburgh, PA, p. 1023 (1976).

7. "High Temperature Pyrolysis of Dimethyl Ether" by D. Aronowitz and D. Naegeli, Int'l. J. of Chem. Kinetics 9, 471 (1977).

8. "Studies of Hydrocarbon Oxidation in a Flow Reactor" by I. Glassman, F. L. Dryer, and R. Cohen, 2nd Int'l. Synp. on Chemical Reaction Dynamics, University of Padua, Italy, 1975.

9. a) "A Numerical Model of Chemical Kinetics of Combustion in a Turbulent Flow Reactor" by C. K. Westbrook, J. Creighton, C. Lund, and F. L. Dryer, J. Phys. Chem. 81, 2542 (1977).

   b) "Detailed Models of Hydrocarbon Combustion" by F. L. Dryer and C. K. Westbrook, Proceedings of the Department of Energy, Division of Power Systems, Workshop on Modelling of Combustion in Practical Systems, Los Angeles, CA, January, 1978.

10. "Flame Ionization Detection of Carbon Oxides and Hydrocarbon Oxygenates" by M. B. Colhet III, D. W. Naegeli, F. L. Dryer, and I. Glassman, Env. Sci. and Tech. 8, 43 (1974).

11. "An Investigation of the Pyrolysis and Oxidation of Ethylene in a Turbulent Flow Reactor" by K. P. Schug, R. J. Santoro, F. L. Dryer, and I. Glassman, Western States Section/Combustion Institute Meeting, Paper No. 78-42 (1978).

12. "Water Addition to Practical Combustion Systems - Concept and Applications" by F.L. Dryer, 16th Symp. (Int'l.) on Combustion, Combustion Institute, Pittsburgh, Pa., p. 279 (1976).

13. "Commends on 'Burning of Water-in-Oil Emulsions' by A. Sjogren" by I. Glassman, 16th Symp. (Int'l.) on Combustion, Combustion Institute, Pittsburgh, Pa., p. 303 (1976).

14. "Combustion" by I. Glassman, Academic Press, New York (1977).

15. "A Review of Oxidation of Aromatic Compounds" by R.J. Santoro and I. Glassman, accepted for publication Combustion Science and Technology (1978).

16. "Kinetics of the Oxidation of Methanol: Experimental Results, Semi-Global Modeling and Mechanistic Concepts" by D. Aronowitz, R.J. Santoro, F.L. Dryer, and I. Glassman, presented at the Seventeenth Symposium (International) on Combustion, University of Leeds, Leeds, England (1978).

17. "Sooting Characteristics of Liquid Pool Diffusion Flames" by Kenneth W. van Treuren, Princeton University Masters Thesis, Department of Mechanical & Aerospace Engineering (1978).

18. "Smoke Point Determinations of Hydrocarbon Diffusion Flames" by K. van Treuren, I. Glassman and K.P. Schug, to be presented at the Fall Technical Meeting of the Eastern States Section of the Combustion Institute, Miami, Florida (1978).

19. "Sooting Characteristics of Gaseous Hydrocarbon Diffusion Flames and the Effect of Additives" by Y.A. Manheimer-Timnat, I. Glassman, R.J. Santoro, and P. Schug, to be presented at the Fall Technical Meeting of the Eastern States Section of the Combustion Institute, Miami, Florida (1978).

20. "Overall and Detailed Kinetic Studies of Propane Pyrolysis" by D. Hautman, R.J. Santoro and I. Glassman, to be presented at the Fall Technical Meeting of the Eastern States Section of the Combustion Institute, Miami, Florida (1978).

21. "Sooting Characteristics of Liquid Pool Diffusion Flames" by K.W. van Treuren, I. Glassman, F.L. Dryer, and K.P. Schug, to be submitted to Combustion Science and Technology.

TABLE 1

Full Mechanism

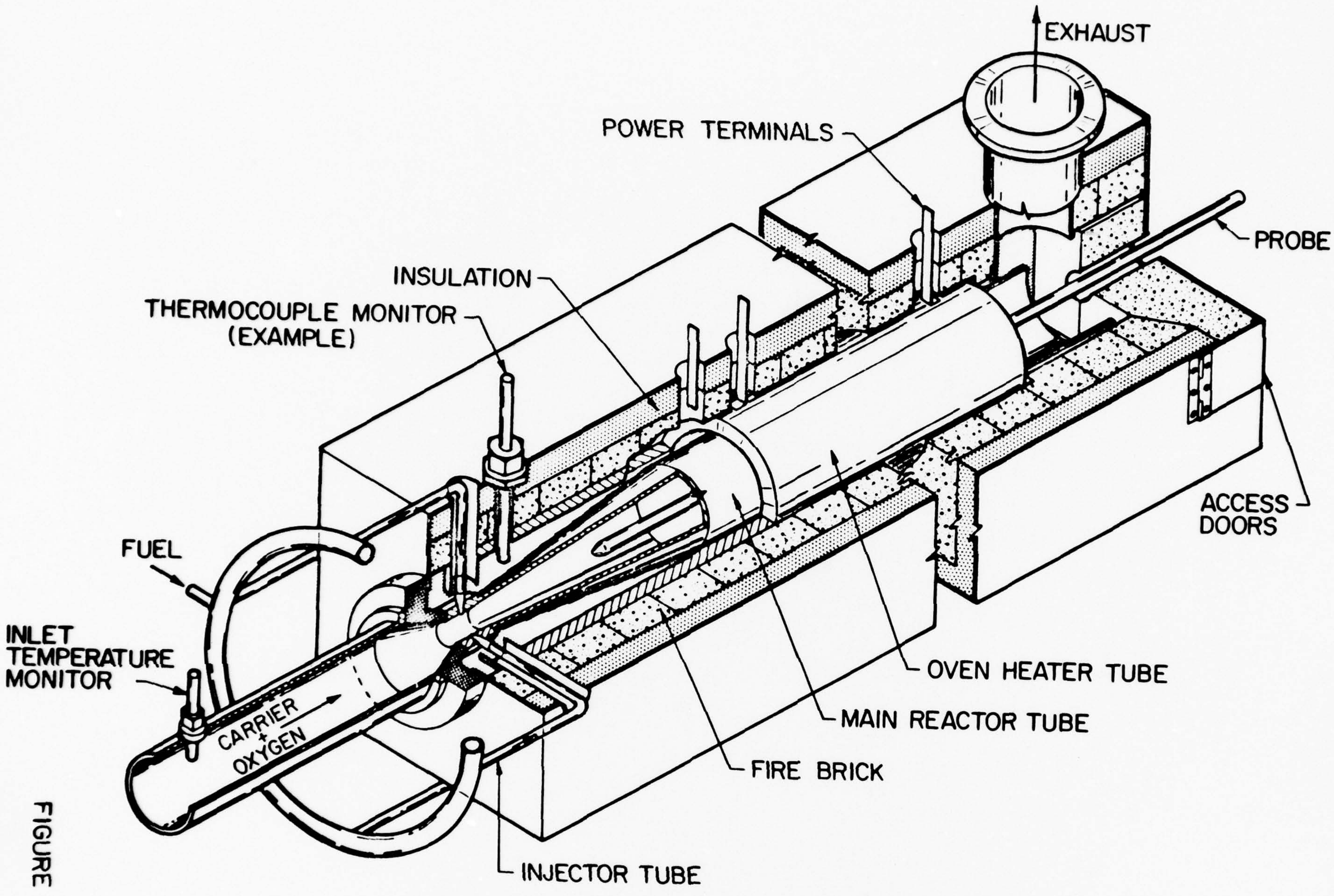
C_3H_8	$\rightleftarrows$	$CH_3 + C_2H_5$	1a,b
$CH_3 + C_3H_8$	$\rightleftarrows$	$CH_4 + iC_3H_7$	2a,b
$CH_3 + C_3H_8$	$\rightleftarrows$	$CH_4 + nC_3H_7$	3a,b
$H + C_3H_8$	$\rightleftarrows$	$H_2 + iC_3H_7$	4a,b
$H + C_3H_8$	$\rightleftarrows$	$H_2 + nC_3H_7$	5a,b
iC_3H_7	$\rightleftarrows$	$H + C_3H_6$	6a,b
iC_3H_7	$\rightleftarrows$	$CH_3 + C_2H_4$	7a,b
nC_3H_7	$\rightleftarrows$	$H + C_3H_6$	8a,b
nC_3H_7	$\rightleftarrows$	$CH_3 + C_2H_4$	9a,b
C_2H_5	$\rightleftarrows$	$C_2H_4 + H$	10a,b
$H + C_3H_6$	$\rightleftarrows$	$C_3H_5 + H_2$	11a,b
$CH_3 + C_3H_6$	$\rightleftarrows$	$CH_4 + C_3H_5$	12a,b
$H + C_2H_6$	$\rightleftarrows$	$H_2 + C_2H_5$	13a,b
$CH_3 + C_2H_6$	$\rightleftarrows$	$CH_4 + C_2H_5$	14a,b
$CH_3 + H_2$	$\rightleftarrows$	$CH_4 + H$	15a,b
$M + H + H$	$\rightleftarrows$	$H_2 + M$	16a,b
$CH_3 + CH_3$	$\rightleftarrows$	C_2H_6	17a,b
$C_2H_4 + M$	$\rightleftarrows$	$C_2H_2 + H_2 + M$	18a,b
$C_2H_4 + M$	$\rightleftarrows$	$C_2H_3 + H + M$	19a,b
$H + C_2H_4$	$\rightleftarrows$	$C_2H_3 + H_2$	20a,b

TABLE 1 (con't.)

Full Mechanism

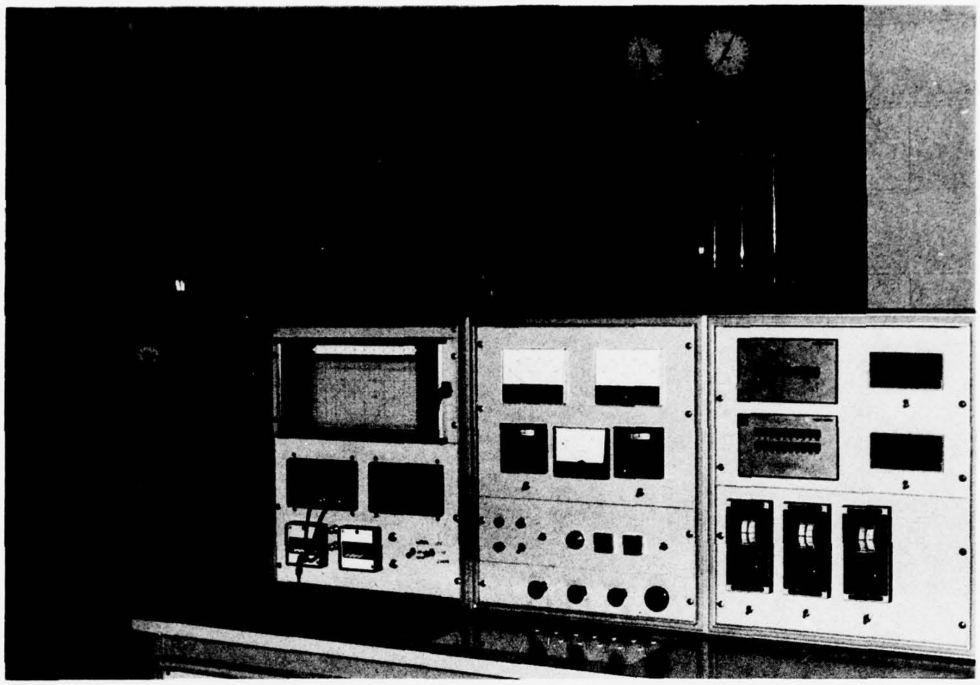
$C_2H_5 + C_2H_3$	$\rightleftarrows$	$C_2H_4 + C_2H_4$	21a,b
$C_2H_3 + M$	$\rightleftarrows$	$C_2H_2 + H + M$	22a,b
$C_2H_3 + C_2H_4$	$\rightleftarrows$	$C_2H_2 + C_2H_5$	23a,b
$C_2H_3 + H$	$\rightleftarrows$	$C_2H_2 + H_2$	24a,b
$C_2H_3 + C_3H_8$	$\rightleftarrows$	$C_2H_4 + iC_3H_7$	25a,b
$C_2H_3 + C_3H_8$	$\rightleftarrows$	$C_2H_4 + nC_3H_7$	26a,b
$C_2H_5 + C_3H_8$	$\rightleftarrows$	$C_2H_6 + iC_3H_7$	27a,b
$C_2H_5 + C_3H_8$	$\rightleftarrows$	$C_2H_6 + nC_3H_7$	28a,b
$iC_3H_7 + C_3H_8$	$\rightleftarrows$	$nC_3H_7 + C_3H_8$	29a,b
$C_3H_8 + C_3H_5$	$\rightleftarrows$	$iC_3H_7 + C_3H_6$	30a,b
$C_3H_8 + C_3H_5$	$\rightleftarrows$	$nC_3H_7 + C_3H_6$	31a,b

JP13 R 4247 72

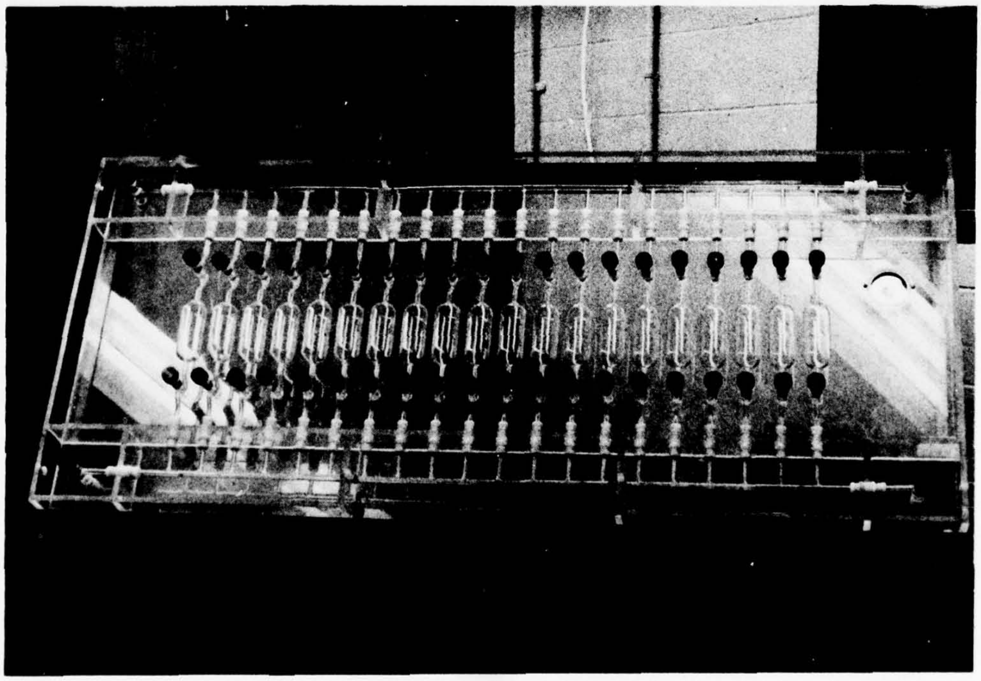


REACTOR ASSEMBLY

FIGURE I

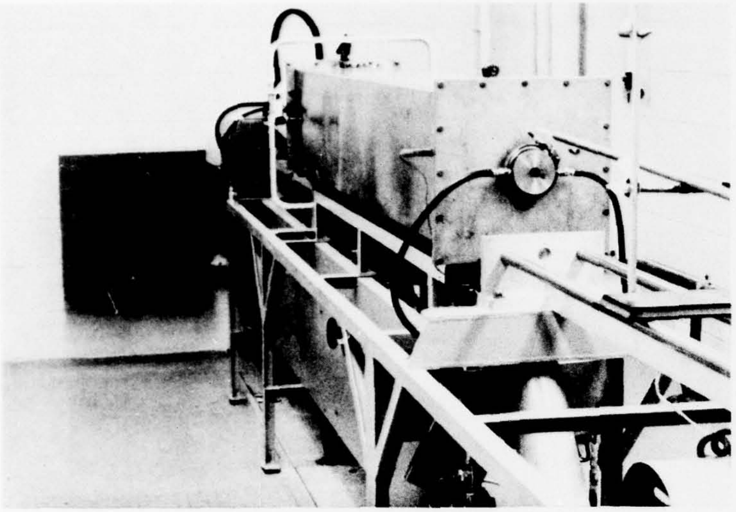


FLOW REACTOR CONTROL PANEL

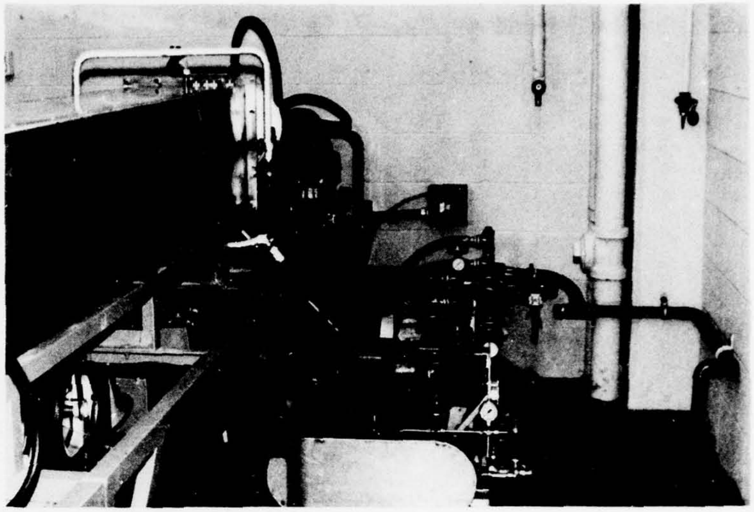


SAMPLING RACK

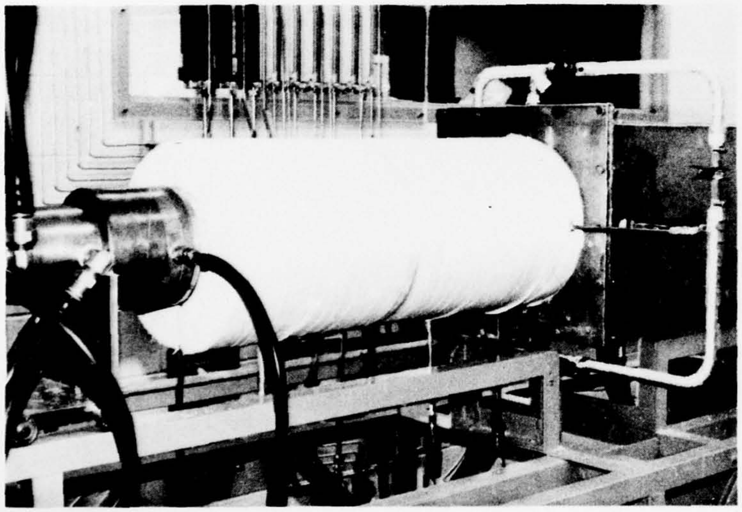
FIGURE 2



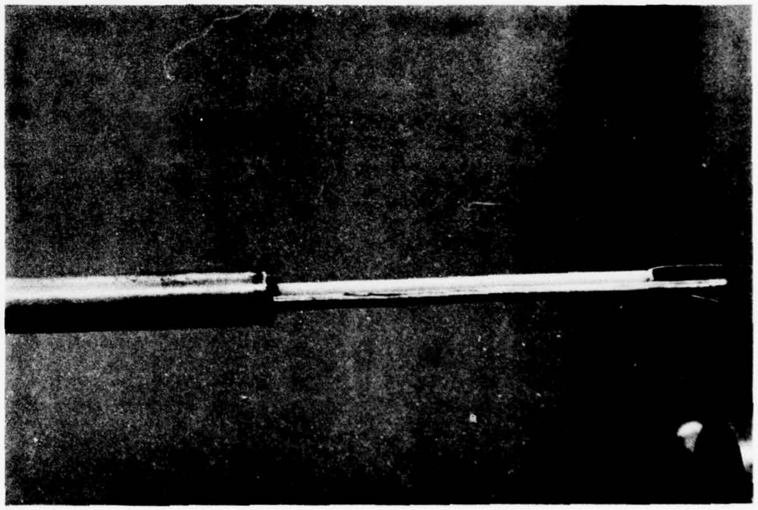
REACTOR ASSEMBLY



REACTOR ASSEMBLY AND COOLING SYSTEM



INLET SECTION AND PLASMA TORCH



SAMPLING PROBE

FIGURE 3

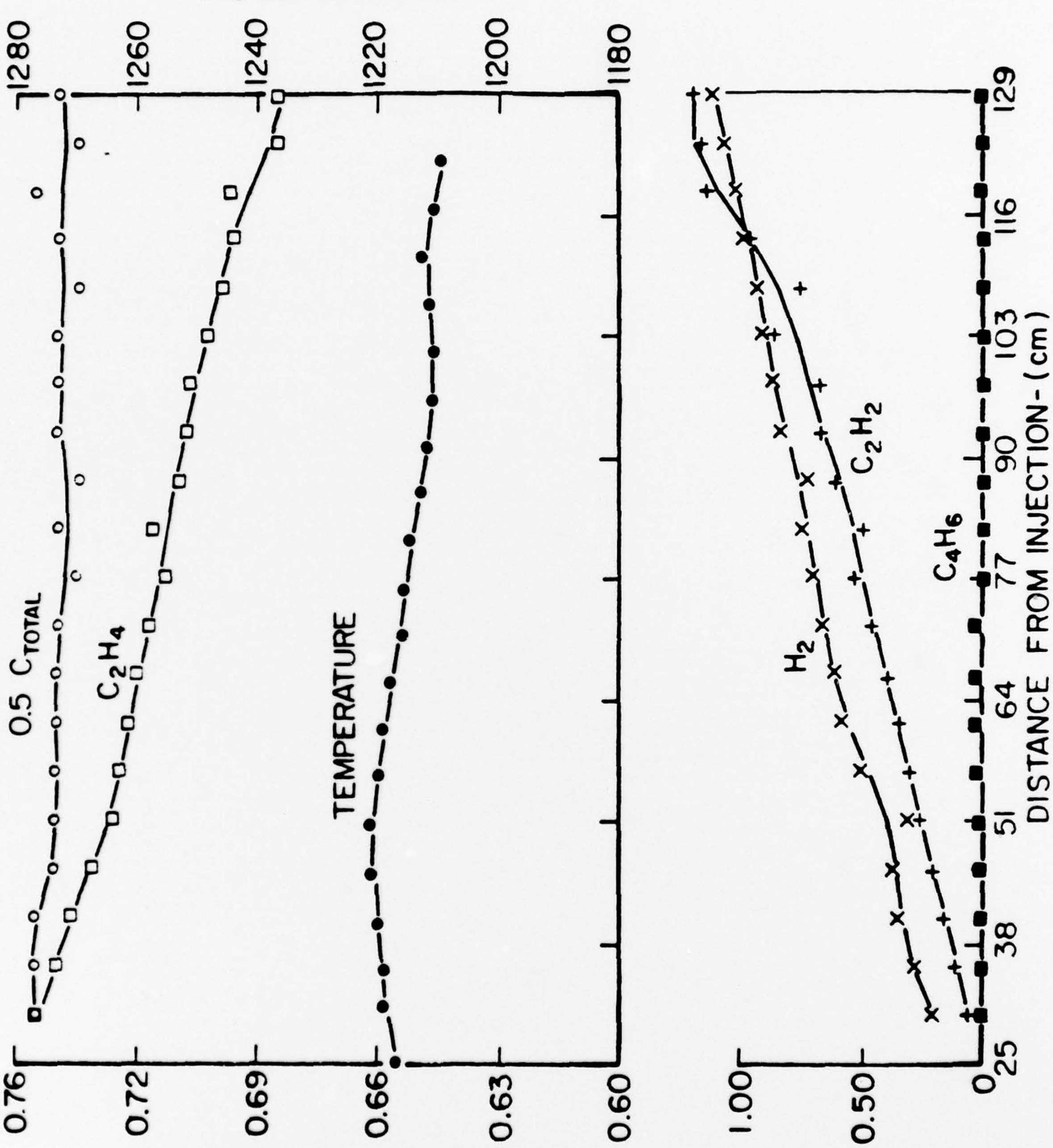

MOLE PERCENT SPECIES
0.76
0.72
0.69
0.66
0.63
0.60
TEMPERATURE (K)
1280
1260
1240
1220
1200
1180
0.5 C_{TOTAL}
C_2H_4
TEMPERATURE
1.00
0.50
0
H_2
C_2H_2
C_4H_6
25
38
51
64
77
90
103
116
129
DISTANCE FROM INJECTION-(cm)

FIGURE 4

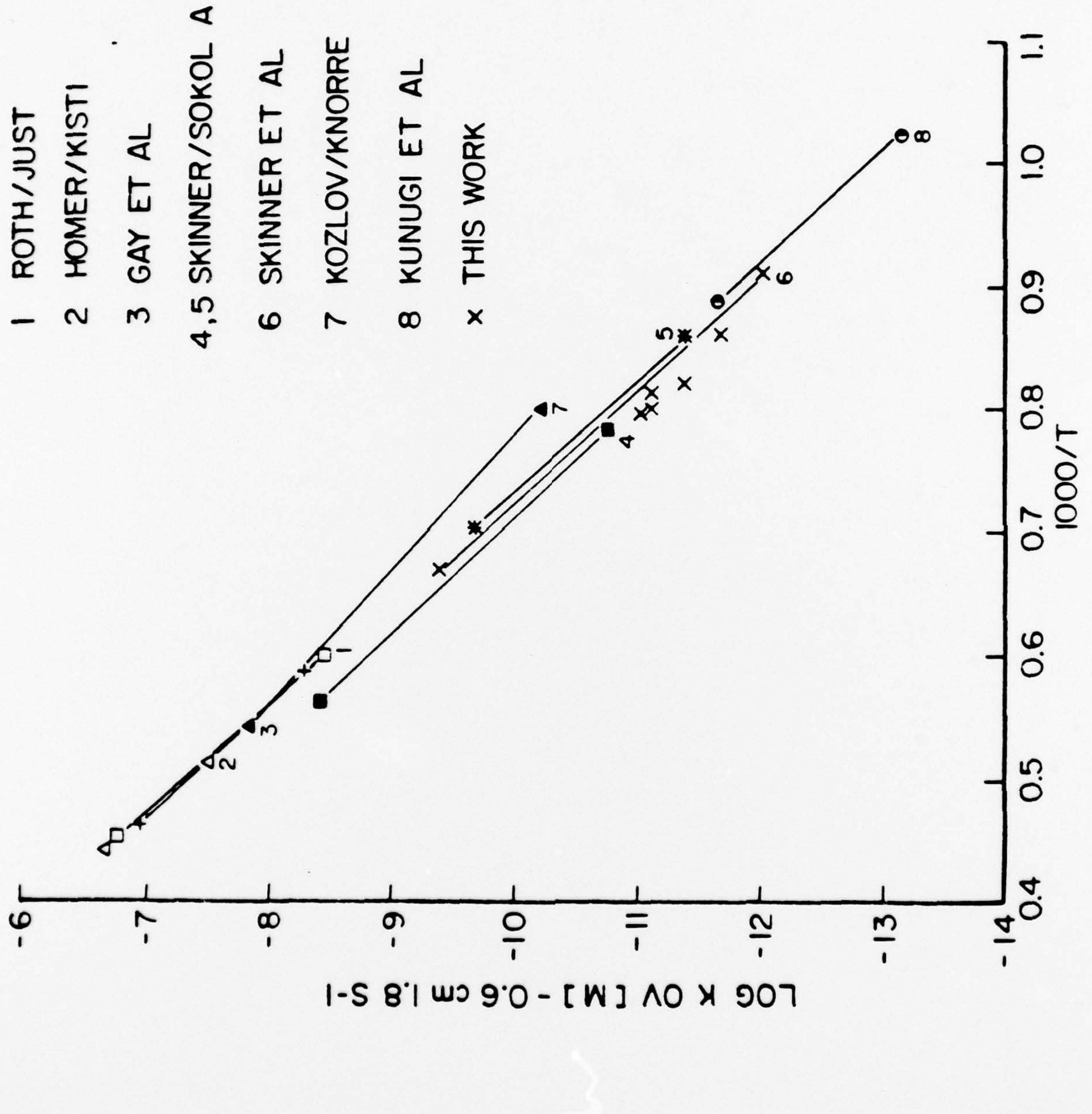

1 ROTH/JUST
2 HOMER/KISTI
3 GAY ET AL
4,5 SKINNER/SOKOL A
6 SKINNER ET AL
7 KOZLOV/KNORRE
8 KUNUGI ET AL
× THIS WORK
LOG K OV [M] - 0.6 cm 1.8 S-1
-6
-7
-8
-9
-10
-11
-12
-13
-14
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1000/T
1
2
3
4
5
6
7
8

FIGURE 5

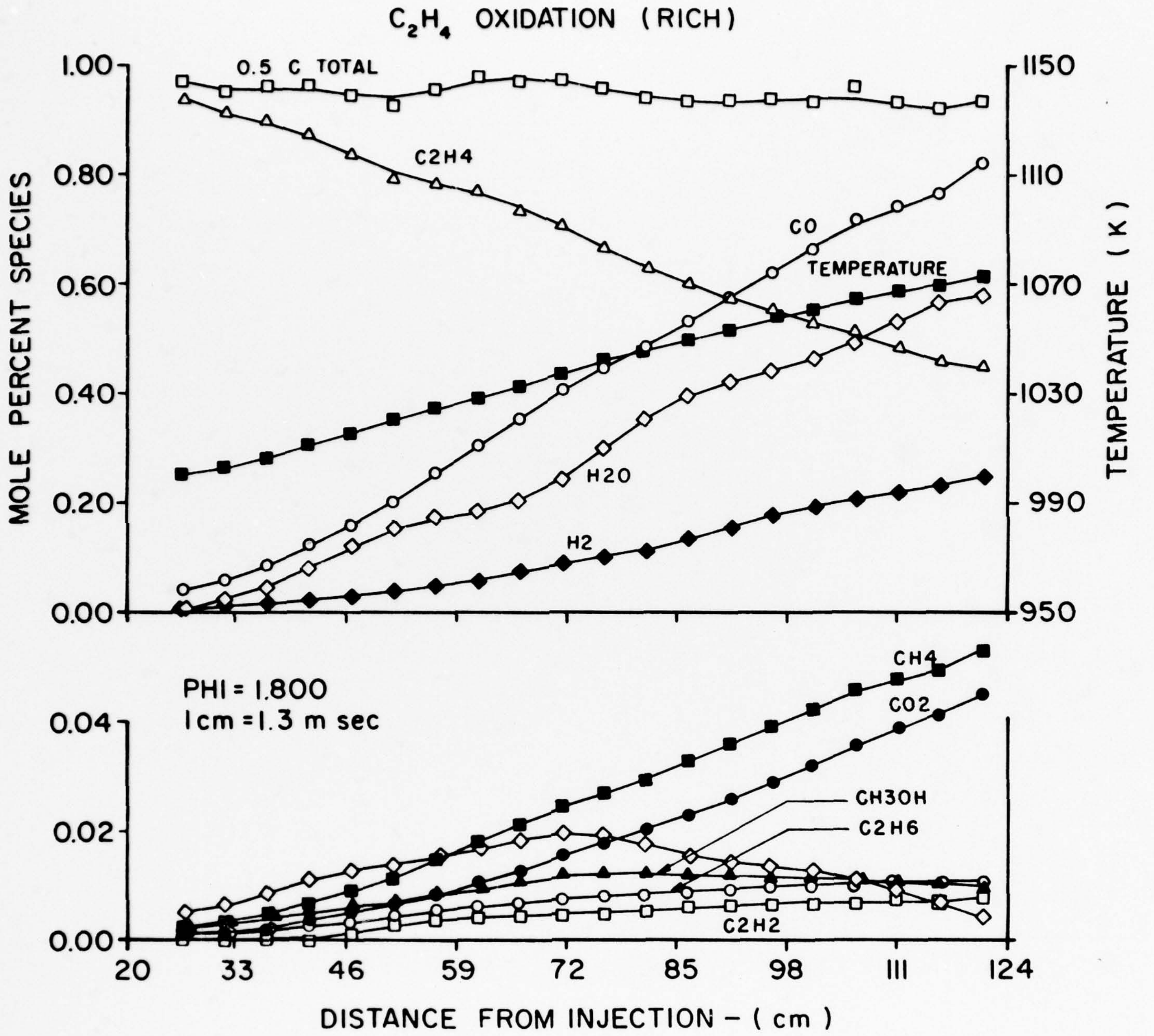

C_2H_4 OXIDATION (RICH)
MOLE PERCENT SPECIES
TEMPERATURE (K)
0.5 C TOTAL
C2H4
CO
TEMPERATURE
H2O
H2
CH4
CO2
CH3OH
C2H6
C2H2
PHI = 1.800
1cm = 1.3 m sec
1.00
0.80
0.60
0.40
0.20
0.00
0.04
0.02
0.00
1150
1110
1070
1030
990
950
20
33
46
59
72
85
98
111
124
DISTANCE FROM INJECTION – (cm)

FIGURE 6

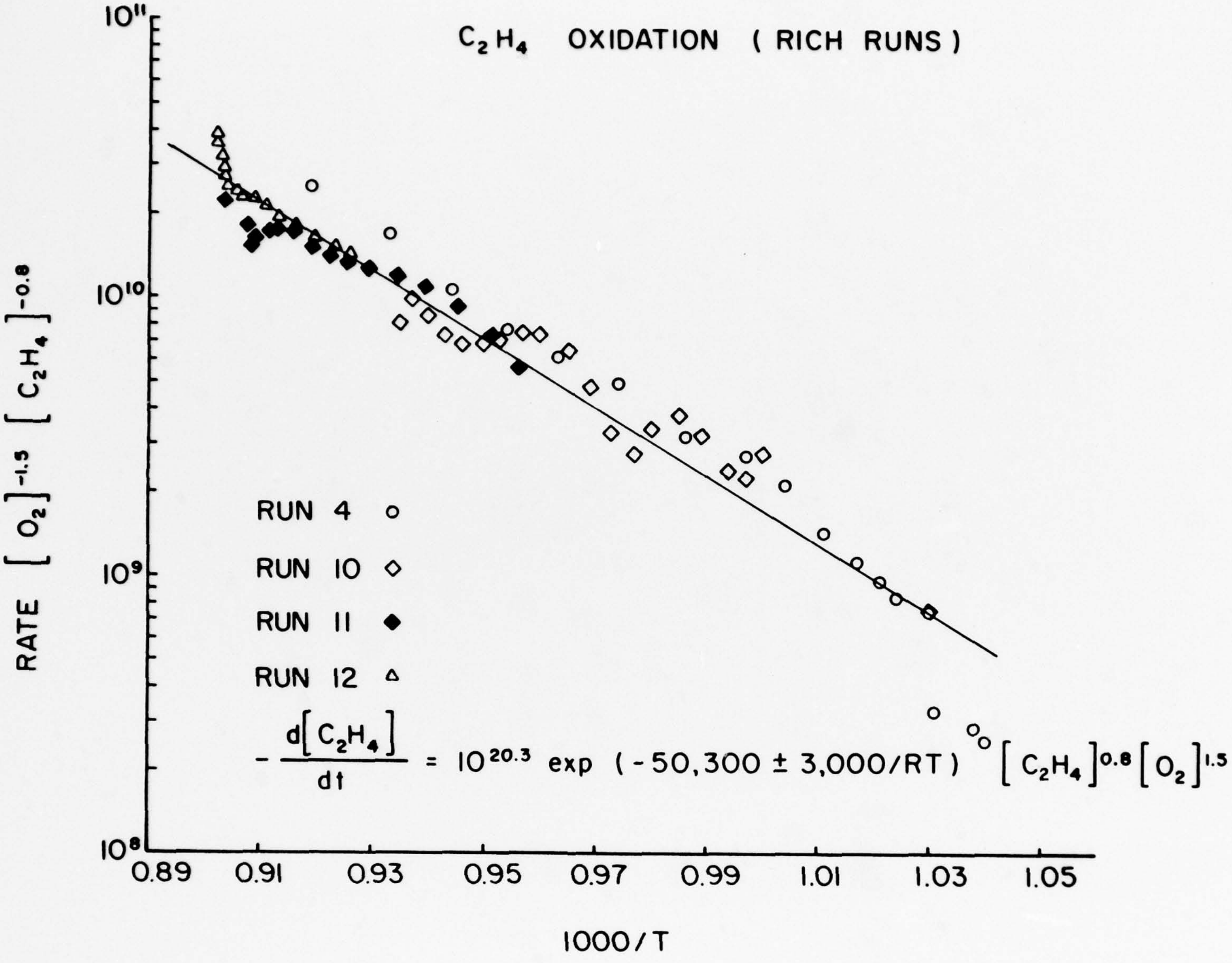

C_2H_4 OXIDATION (RICH RUNS)
RATE $[O_2]^{-1.5}$ $[C_2H_4]^{-0.8}$
10^{11}
10^{10}
10^{9}
10^{8}
0.89
0.91
0.93
0.95
0.97
0.99
1.01
1.03
1.05
1000/T
RUN 4 ○
RUN 10 ◇
RUN 11 ◆
RUN 12 △
$-\frac{d[C_2H_4]}{dt} = 10^{20.3} \exp(-50{,}300 \pm 3{,}000/RT)\,[C_2H_4]^{0.8}[O_2]^{1.5}$

FIGURE 7

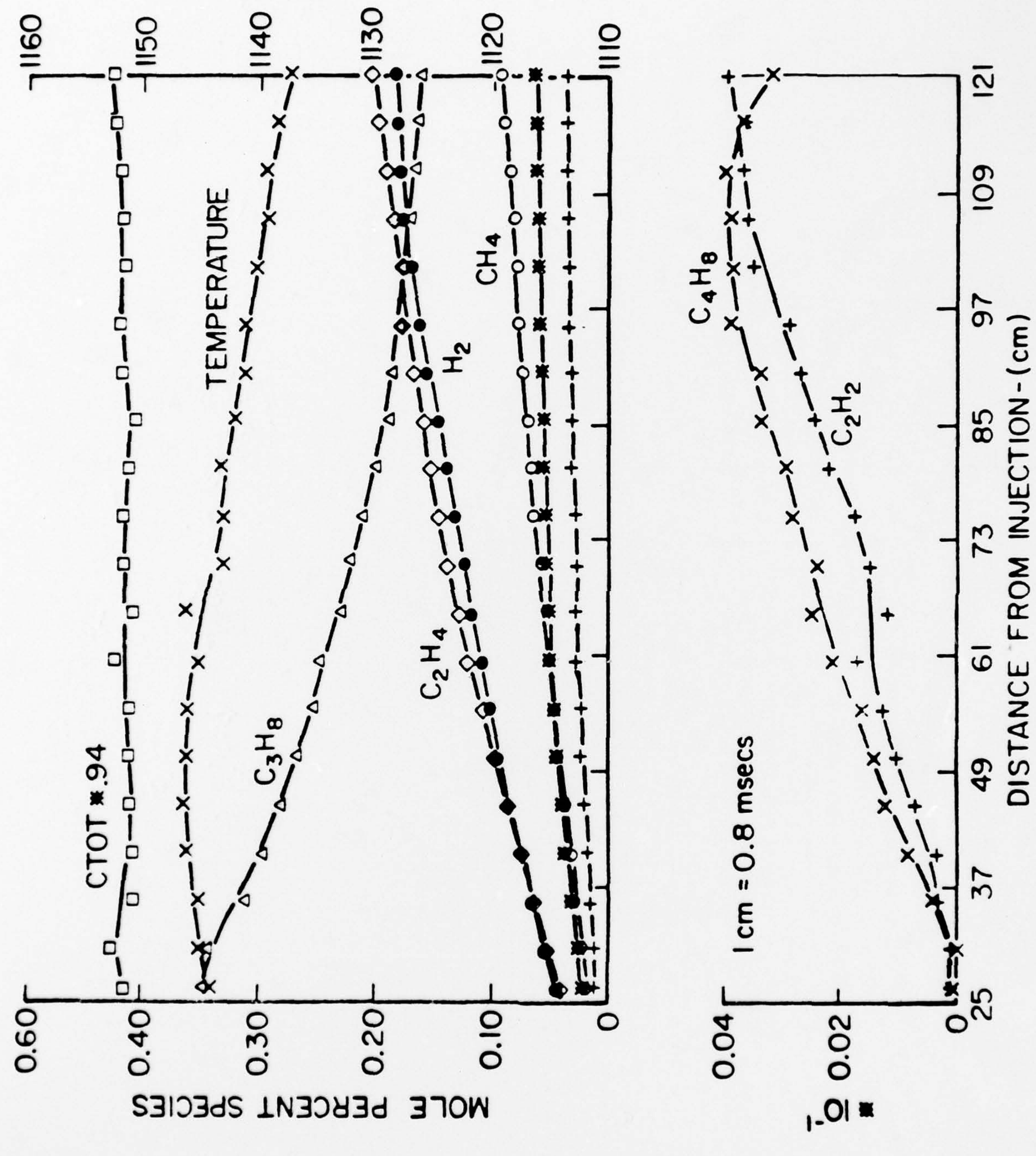
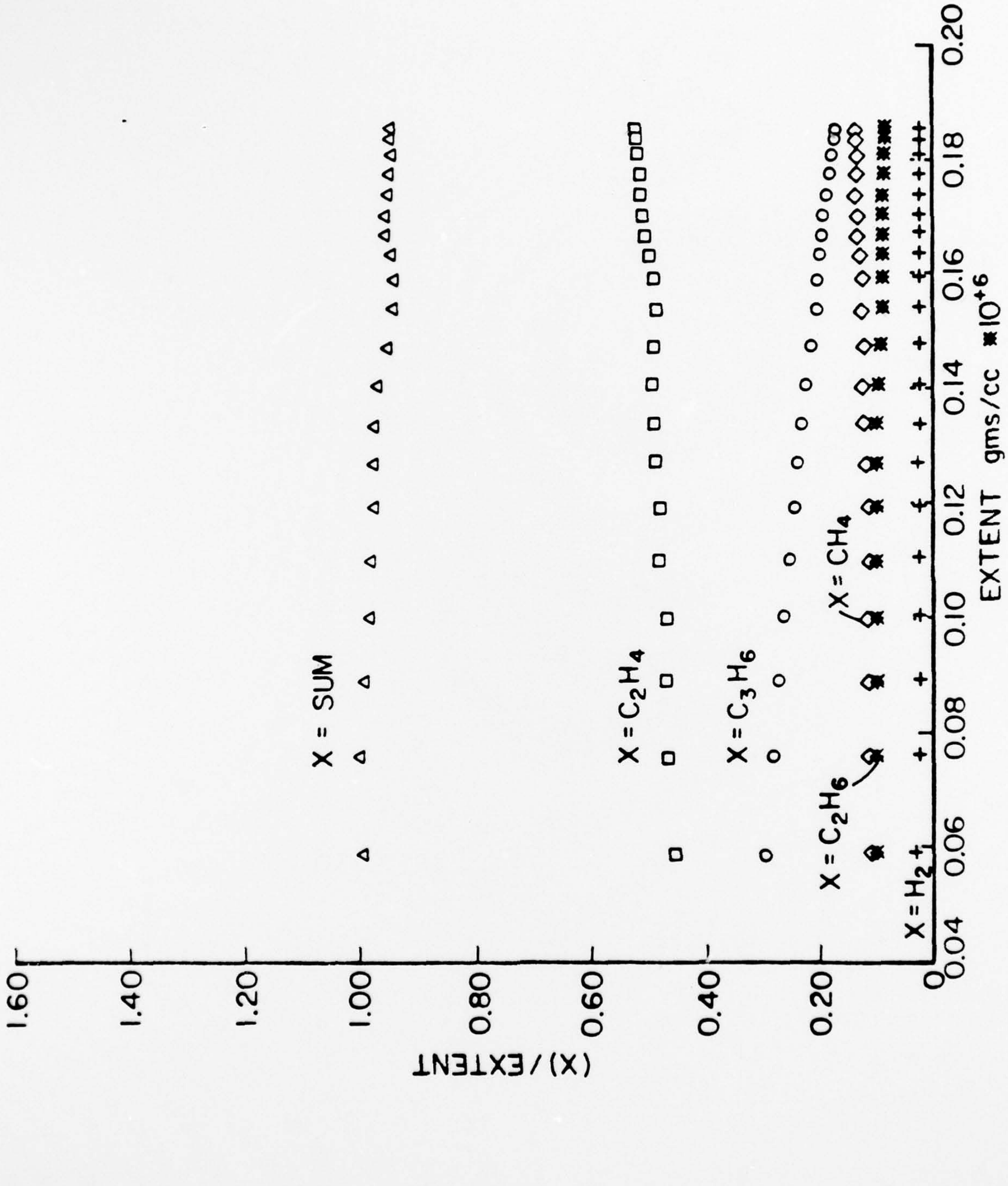
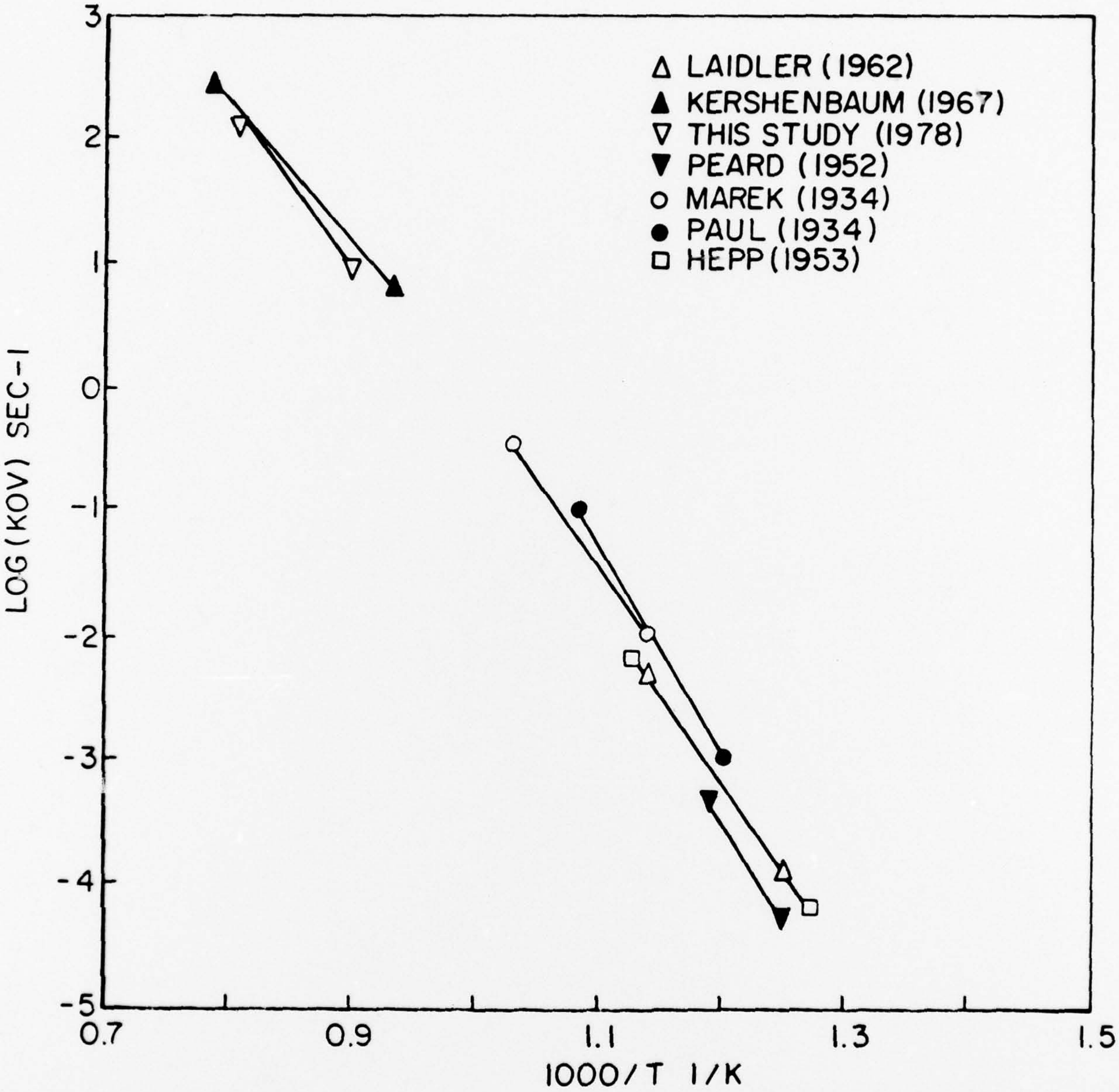

MOLE PERCENT SPECIES
0.60
0.40
0.30
0.20
0.10
0
TEMPERATURE (K)
1160
1150
1140
1130
1120
1110
CTOT * .94
TEMPERATURE
C_3H_8
C_2H_4
H_2
CH_4
0.04
0.02
0
* 10^{-1}
1 cm = 0.8 msecs
C_4H_8
C_2H_2
25
37
49
61
73
85
97
109
121
DISTANCE FROM INJECTION-(cm)

FIGURE 8



(X)/EXTENT
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20
EXTENT gms/cc $*10^{+6}$
X = SUM
X = C_2H_4
X = C_3H_6
X = C_2H_6
X = CH_4
X = H_2

FIGURE 9



PROPANE PYROLYSIS

FIGURE 10

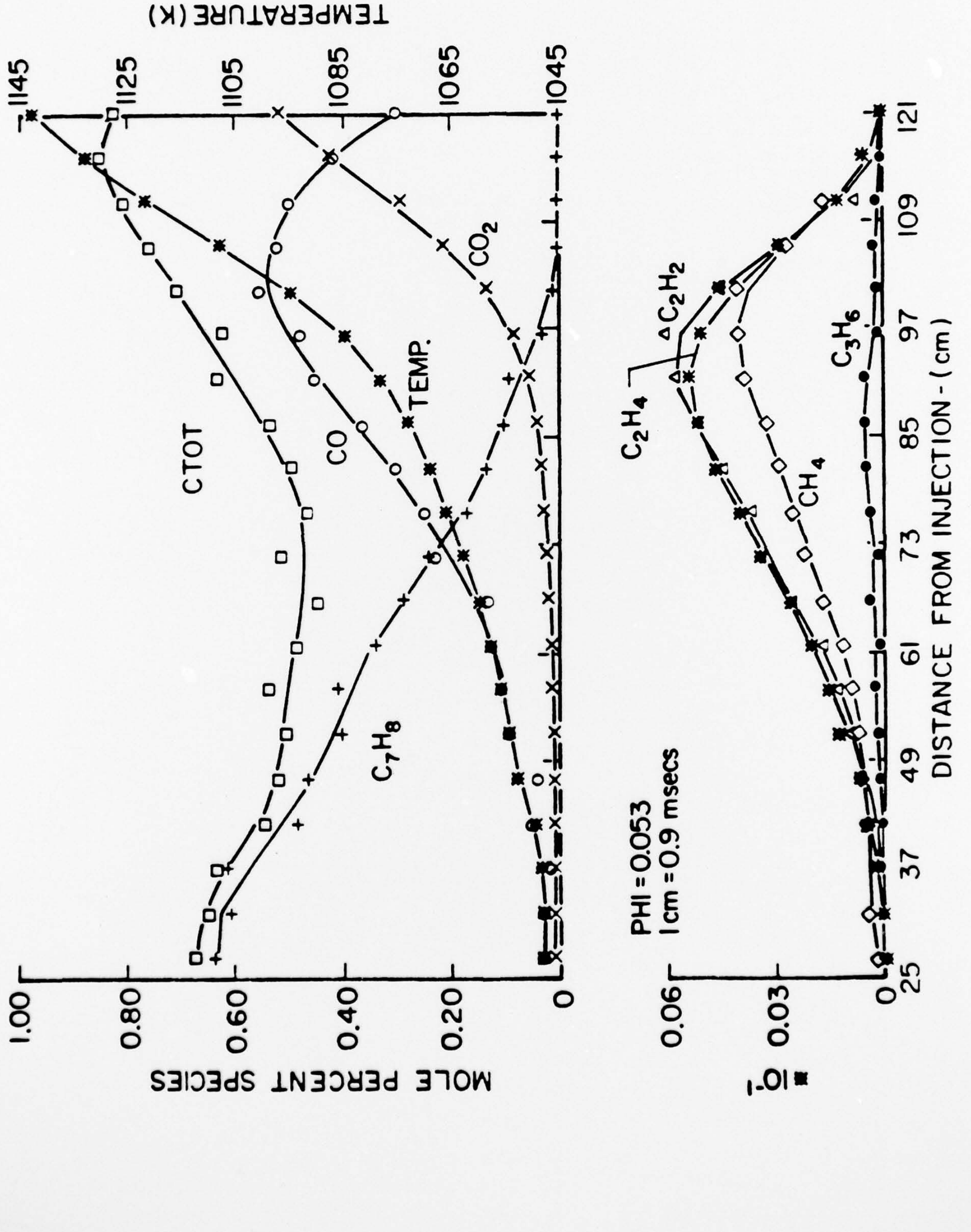
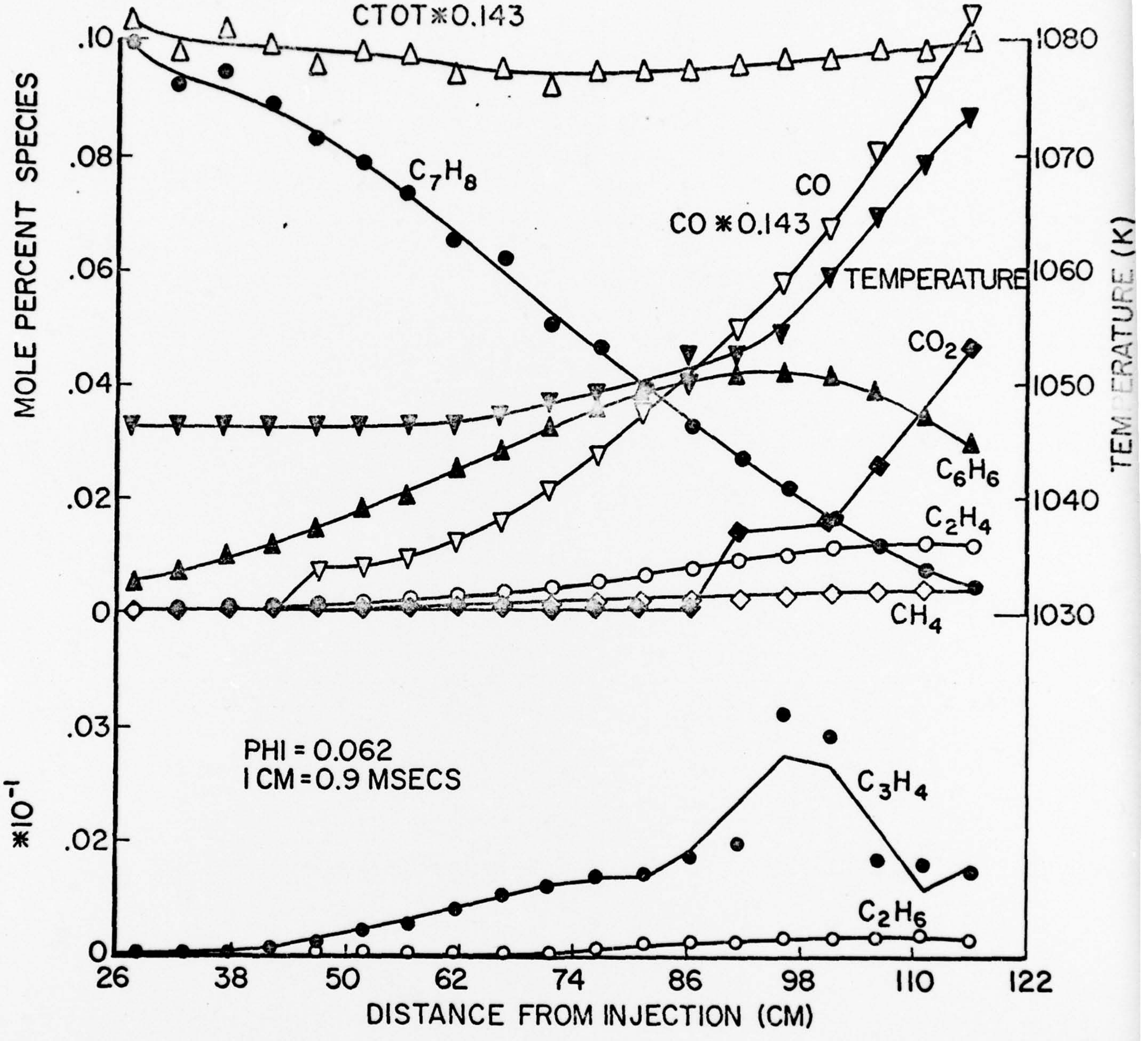
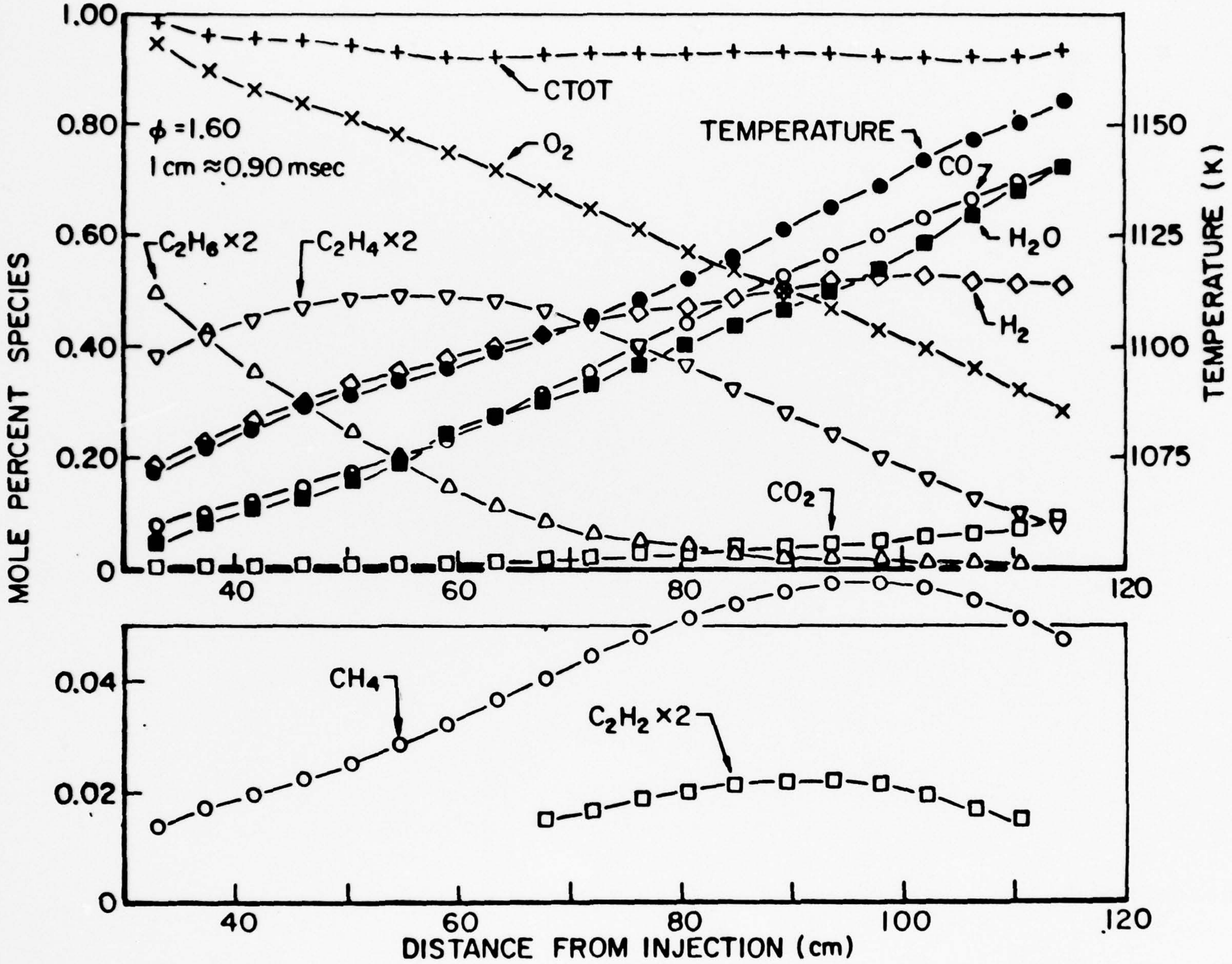

MOLE PERCENT SPECIES
1.00
0.80
0.60
0.40
0.20
0
TEMPERATURE (K)
1145
1125
1105
1085
1065
1045
CTOT
CO
TEMP.
CO_2
C_7H_8
0.06
0.03
0
$\times 10^{-1}$
PHI = 0.053
1cm = 0.9 msecs
C_2H_4
C_2H_2
CH_4
C_3H_6
25
37
49
61
73
85
97
109
121
DISTANCE FROM INJECTION - (cm)

FIGURE *11*



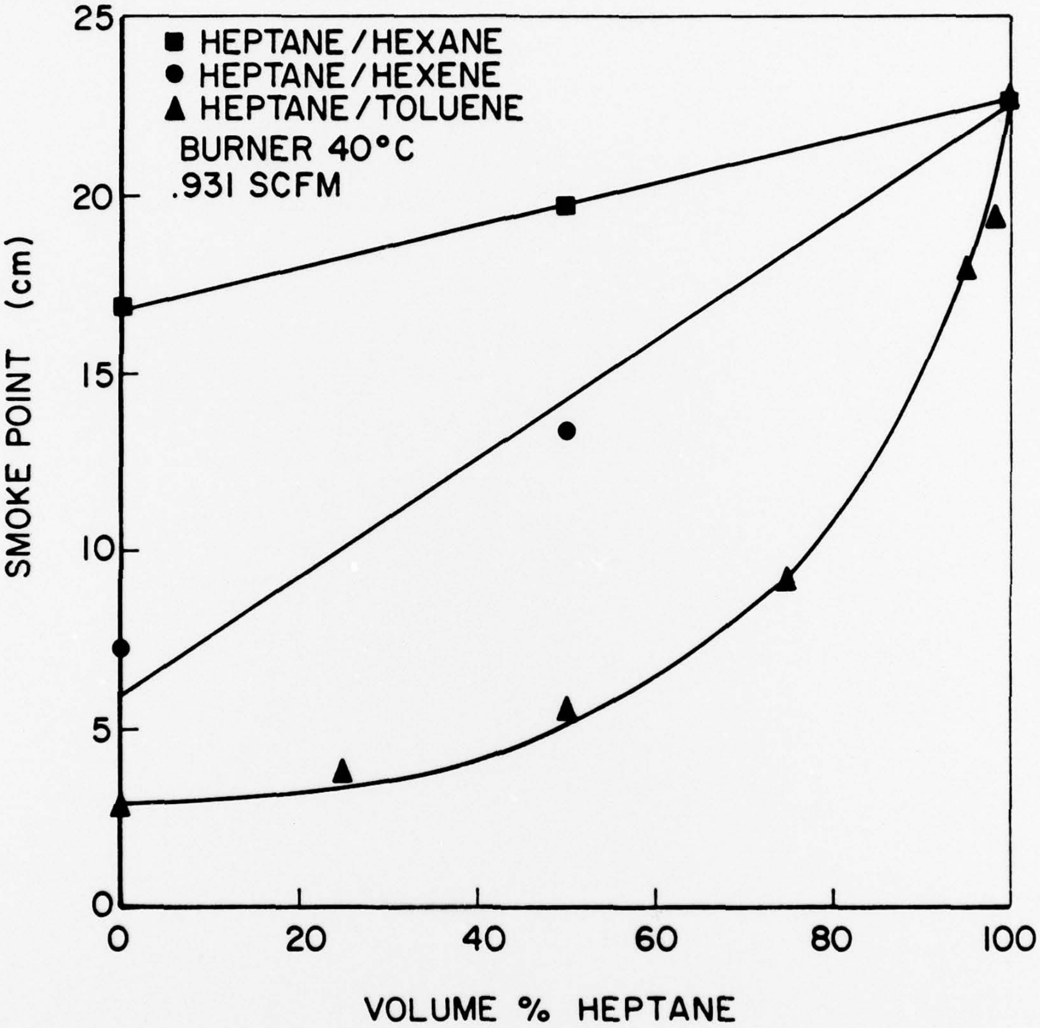
TOLUENE OXIDATION

FIGURE 12



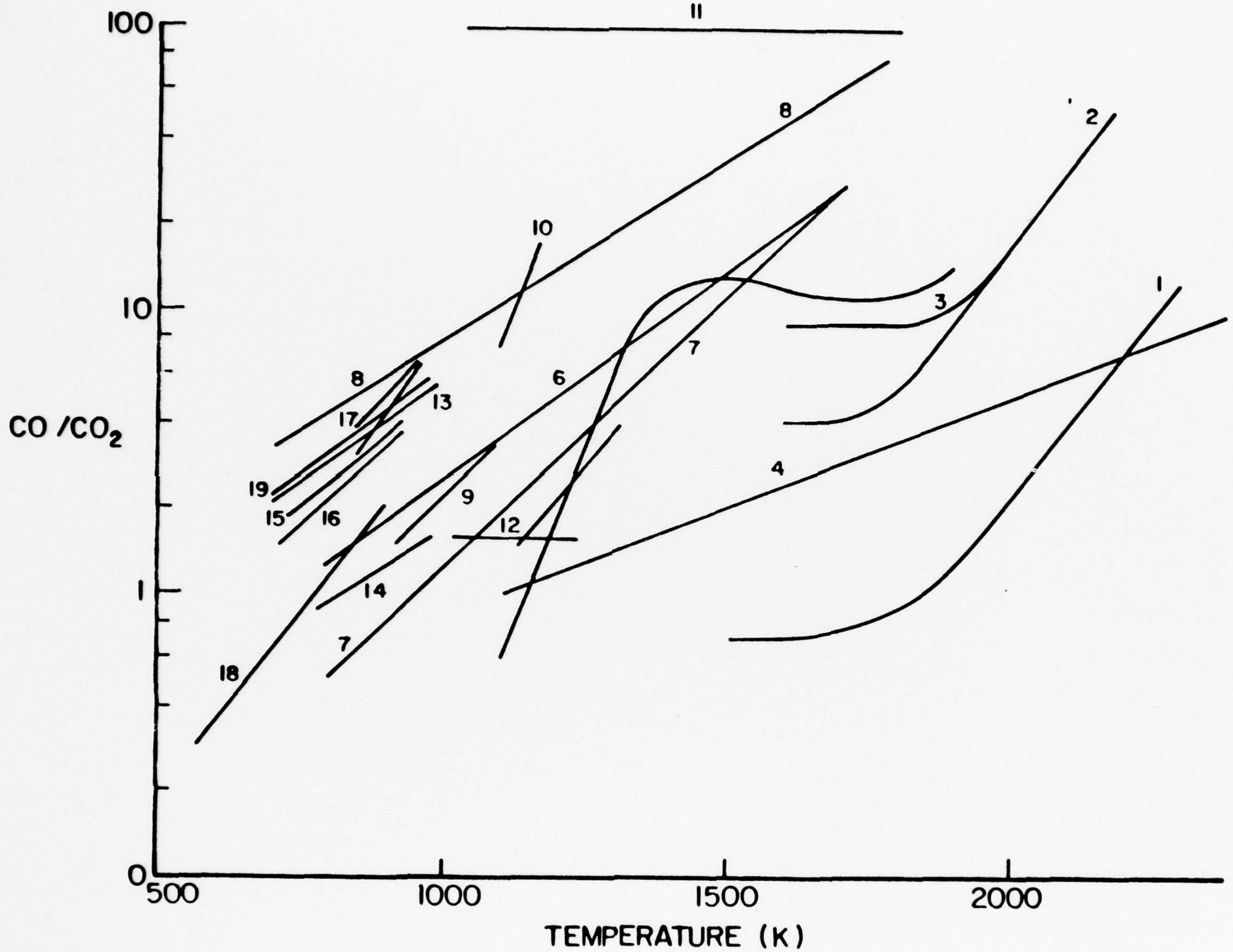
CHEMICAL COMPOSITION OF SPREAD ETHANE- O_2 REACTION

FIGURE 13



Smoke Points of Fuel Mixtures

FIGURE 14



SURVEY OF EXPERIMENTAL RESULTS (CO/CO$_2$) RATIO IN CARBON OXIDATION

FIGURE 15

Reference Legend for Figure 15

1. Day, Walker and Wright: "Industrial Carbon and Graphite", 348, 1958 (petroleum coke, graphitized lampblack and anthracite).
2. Day et al. (anthracite-based carbon).
3. Day et al. (lampblack-based carbon).
4. Olander, Sickhaus, Jones and Schwartz: JCP 57, 403, 1972 (Pyrolytic graphite, prismatic plane).
5. Allendorf and Rosner, Carbon 7, 515, 1969.
6. Rossberg: Z. Elektrochem. 60, 952, 1956 (electrode carbon A).
7. Rossberg: (electrode carbon B).
8. Arthur: Traus. Far, Soe. 47, 164, 1951 (with PO Cl_3).
9. Wicke: "5th Synp. on Combustion", 245, 1955 (no PO Cl_3).
10. Wicke: (with PO Cl_3).
11. Olander et al.; JCP 57, 421, 1972 (pyrolytic graphite, based plane).
12. Goard and Mulcahy: Carbon 5, 137, 1967.
13. Laine, Vastola and Walker: "Proe. 5th Conf. on Carbon", Vol. II, 211, 1963.
14. Henchamps et Duval: Carbon 4, 243, 1966 (graphite P).
15. Bonnetain, Duval and Letart: "Proe. 4th Conf. on Carbon", 107, 1960 (E = 6K cal).
16. Bonnetain et al. (E = G-2 K cal, AFCI and NC graphites).
17. Laine, Vastola and Walker: JPC 67, 2030, 1963.
18. Lang, deNoblet and Brie: Carbon 7, 433, 1969.
19. Phillips, Vastola and Walker: Carbon 8, 205, 1970 (lower line more surface oxide).

PROFESSIONAL RESEARCH PERSONNEL ASSOCIATED WITH THE RESEARCH EFFORT

During the past contract (Oct. 1, 1977 through Sept. 30, 1978) the following personnel have been associated with the program:

Principal Investigators

I. Glassman		1/4 time summer
F.L. Dryer	2/9 time 9 mos. academic,	1/3 time summer

Professional Research Staff

R.J. Santoro	1/2 time 12 mos.
A.C. Fernandez-Pello	1/4 time 12 mos.

Visiting Research Faculty and Fellows

Y. Timnat	Full-time 12 mos.
K.P. Schug*	1/2 time 12 mos.

Degrees Awarded

Lt. K. van Treuren received his Masters Degree effective September 1, 1978. His thesis was entitled, "Sooting Characteristics of Liquid Pool Diffusion Flames."

Interactions (coupling activities)

The following presentations have resulted from research performed this year:

(1) "An Investigation of the Pyrolysis and Oxidation of Ethylene in a Turbulent Flow Reactor" presented at the Western States Section/Combustion Institute Meeting (1978).

(2) "Smoke Point Determinations of Hydrocarbon Diffusion Flames" to be presented at the Eastern State Section/Combustion Institute Meeting (1978).

(3) "Sooting Characteristics of Gaseous Hydrocarbon Diffusion Flames and the Effects of Additives" to be presented at the Eastern States Section/Combustion Institute Meeting (1978).

(4) "Overall and Detailed Kinetic Studies of Propane Pyrolysis" to be presented at the Eastern States Section/Combustion Institute Meeting (1978).

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* Dr. Schug's efforts on this program have been at no cost to AFOSR.