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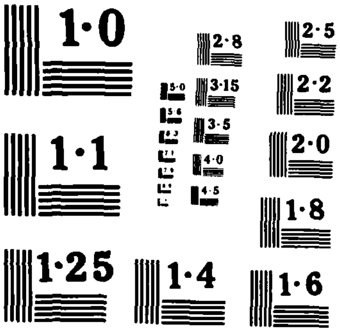

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PREIGNITION OXIDATION CHARACTERISTICS
OF HYDROCARBON FUELS

Final Report
15, OCTOBER 14, 1984
April 1980 - ~~January 1985~~

N.P. Cernansky, R.S. Cohen and R.D. Wilk

July 1985

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Principal Investigators: N.P. Cernansky and R.S. Cohen

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Research supported by the U.S. Army Research Office
ARO Contract No. DAAG 29-80-C-0112
Reference No. P-16957-E

ABSTRACT

A research program to study the preignition oxidation characteristics of hydrocarbon fuels has been carried out. A static reactor test facility and gas chromatographic analysis techniques were used to assess the preignition oxidation chemistry by determining the stable reaction intermediates and products formed during the preignition process. Comprehensive studies were made of the oxidation of propane and propene at low and intermediate temperatures (550–750 K) and at subatmospheric pressures. The experimental results for each of these fuels demonstrated a clear transition in the oxidation chemistry from a low temperature regime to an intermediate temperature regime, separated by a region of negative temperature coefficient. The main characteristics and features of the oxidation mechanisms were determined for each fuel in each temperature regime. Increasing the vessel surface-to-volume ratio had the effect of enhancing heterogeneous termination, but did not affect the main reaction paths of the mechanism. The experimental results for propene were used to modify and extend the high temperature mechanism of Westbrook and Pitz to low and intermediate temperatures. Studies were also made of the preignition behavior of dodecane and binary mixtures of dodecane and the aromatic component tetralin. Addition of the tetralin to dodecane had the overall effect of decreasing the ignition tendency, although the magnitude of this effect was not proportional to the amount added.

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I. INTRODUCTION AND PROGRAM OVERVIEW

A. INTRODUCTION

The study of the chemical processes which lead up to autoignition are of primary importance in developing a fundamental understanding of the overall ignition behavior of hydrocarbon fuels. Autoignition is a complex process involving preignition reactions which lead up to the point of hot ignition. This is the point at which energy is liberated at a sufficient rate to sustain combustion in the absence of an external energy source. It is generally associated with rapid rates of temperature and pressure rise. For the case of autoignition, then, it is the preignition chemical behavior of the system which determines whether or not ignition occurs.

An integral and controlling part of the autoignition process is the oxidation chemistry. The oxidation chemistry is important because it determines the reaction intermediates, the heat release rate, and the ultimate products of combustion. It is, however, very complex and involves a reaction mechanism, which consists of a large number of concurrent and competing chemical reactions, with a correspondingly large number of chemical species. Furthermore, the reaction mechanism is very dependent on the physical conditions of the combustion environment. Different reaction paths can be dominant at different temperatures, pressures, and equivalence ratios.

Reaction mechanisms are especially sensitive to temperature. In general, aliphatic hydrocarbon oxidation chemistry can be divided into three main temperature regimes: (1) low temperature (<650K); (2) intermediate temperature (650-1000 K); and (3) high temperature (>1000 K). Each temperature regime is characterized by differences in the oxidation chemistry, such as the abundant radical species and the types of reaction products formed. For example, the oxidation chemistry in the low temperature regime is dominated by reactions involving peroxy radicals which ultimately lead to the formation of oxygenated hydrocarbon products. Also, under certain conditions, these low temperature reactions can lead to cool-flames and two-stage ignition. In the intermediate temperature range reactions involving the hydroperoxyl radical are dominant and can lead to non-oxygenated hydrocarbon products such as lower alkanes and alkenes. The chemistry in this temperature range can lead to single-stage hot ignition. Finally, at the high temperatures, the most abundant radical is the hydroxyl radical although H and O radicals can also be dominant, depending on the stoichiometry. In this high temperature regime the chemistry is extremely fast, with rapid rates of heat release.

In relating these different combustion regimes to actual combustion devices, it is realized that most actual combustors operate mainly in the high temperature regime. However, there are generally large temperature gradients in these devices during system operation, and the fuel passes through and can spend considerable time in one or both of the lower temperature regimes. In particular, the autoignition process in diesel engines is initiated at these lower temperatures. This is also the case for end gas autoignition in the cylinders of SI engines, which leads to engine knock. Consequently, the autoignition processes in these actual combustion devices typically depends on the low and intermediate temperature preignition oxidation chemistry.

It is desirable to be able to model the chemical and physical processes in actual combustion systems. In order to do this, reliable submodels of the hydrocarbon oxidation chemistry are needed. Several detailed chemical kinetic mechanisms have been developed for relatively simple low molecular weight fuels ranging from hydrogen to butane. These have been reviewed recently by Westbrook and Dryer (1984). The mechanisms for the lighter fuels such as H_2, CO, CH_4, and C_2H_4 are used as building blocks in a hierarchical scheme and incorporated into the mechanisms for fuels such as propane and butane. Many of these kinetic models were constructed to reproduce results from the high temperature regime, obtained from experiments using shock tubes (Burcat et al., 1971), flames (Kaiser et al., 1985), and high temperature flow reactors (Hautman et al., 1981). Thus, they are primarily applicable only for temperatures above about 1000 K.

For a chemical kinetic reaction mechanism to be effective for combustor modeling, it should be applicable over a wide range of conditions. Such a mechanism was termed a comprehensive kinetic mechanism by Westbrook and Dryer (1981). Development of a comprehensive mechanism requires experimental verification over a range of conditions. This usually means using several different experimental systems, each suitable for a particular reaction regime. Thus, in order to apply the aforementioned models over the entire operating range of various combustion devices, especially to the autoignition process, they must be extended and validated to include the lower temperature (<1000 K) reaction regimes as well. Once this is done, kinetics models can be extended further, using the hierarchical approach, and eventually applied to higher molecular weight fuels and to pure fuel mixtures which are characteristic of actual full-boiling range fuels in use today. Ultimately, the models can be extended to include the low grade and synthetic fuels which will be used in the future.

Detailed chemistry studies on higher molecular weight fuels, thus far, have been limited. This is due mainly to the complexities encountered when attempting to chemically quantify the multitude of intermediate and product species which are formed from high molecular weight hydrocarbons. Some studies on the detailed chemistry of aromatic and aliphatic hydrocarbons up to C_8 though, have been made recently by the Princeton group (Venkat et al., 1983; Brezinsky and Dryer, 1985; and Litzinger et al., 1984). Many phenomenological studies have also been made of individual higher molecular temperature oxidation of propane. It can be seen in Figs. 3 and 4 that the pressure histories of the reactions have the characteristic S-shape, displaying a well defined induction period, during which there is little pressure change. This is followed by a rapid exponential increase and finally a leveling off in the pressure. Since the rate of change of pressure can be used as a measure of the overall rate of reaction, it can be seen from the slope of the pressure traces that the overall rate starts out very slow, accelerates to a maximum and then slows again.

The corresponding temperature profiles (Figs. 5 and 6) show a slow increase in the temperature at the center of the vessel as the reaction progresses. A maximum is reached at about 10-40 degrees above the initial temperature (depending on the initial conditions). This is then followed by a decrease in temperature back down to the initial temperature. Since the system is non-adiabatic, the rate of temperature change is only a measure of the net heat release, that is, the heat produced by the reaction less the heat lost to the vessel walls. The time at which the maximum temperature occurs corresponds to the point in the reaction where the heat loss to the walls equals the heat generated by the reaction.

The induction period, τ, is defined here as the time period from the admission of the mixture to the reaction vessel to the onset of the rapid pressure rise and is measured by extending the tangent at the inflection point in the pressure profile down to the line of initial pressure. The induction period is, therefore, a measure of the characteristic time preceding the rapid acceleration of the reaction. From a chemistry standpoint, during this period the fuel begins to oxidize very slowly, gradually producing a quasi-stable branching intermediate. This intermediate then breaks down into free radicals which accelerate the reaction. As the reactants are depleted, the study of propane oxidation carried out during one phase of this research project.

One of the main objectives for this particular study was to verify the operation of the experimental system. Since there is an ample supply of data for propane in the low temperature regime, this fuel was well suited for that purpose. Another objective of this work was to supplement the existing knowledge of the low temperature oxidation behavior of propane. Much of the earlier work was done in the 1930's-1950's before the development of sophisticated gas chromatographic analysis techniques. Today, species measurements can be made more easily and with more accuracy. In addition to identifying important reaction intermediates and products, the reactions can actually be followed in time. A set of species concentration profiles can then be obtained for each experimental condition, from which the detailed oxidation behavior of the fuel can be determined and theoretical models verified.

Finally the most important objective of this work was to determine the characteristics of the oxidation chemistry in the intermediate temperature regime and to distinguish it from that of the low temperature regime. The chemistry in the intermediate temperature reaction regime is most important to the autoignition process but, to date, has received little attention.

In the propane studies, the effects of initial temperature, initial pressure, equivalence ratio, and vessel surface-to-volume ratio on the pre-ignition oxidation behavior was examined. The characteristics of the oxidation chemistry in each of these reactions regimes were determined.

B. EXPERIMENTAL RESULTS AND DISCUSSION

1. Cool Flames and Negative Temperature Coefficient

The experimental results confirm the autocatalytic nature of the low

III. PREIGNITION OXIDATION CHARACTERISTICS OF PROPANE

A. INTRODUCTION

As mentioned previously, the autoignition process in engines is initiated at relatively low temperatures (<1000 K). The oxidation of aliphatic hydrocarbons at these lower temperatures is a complex process involving degenerate free radical chain branching reactions. Under certain conditions these reactions can lead to the formation of cool flames and, in some instances, the occurrence of two-stage ignition. Also associated with the oxidation of hydrocarbons at these temperatures is the negative temperature coefficient of reaction rate. For many hydrocarbons there exists a temperature range (50-100 degrees) usually falling between about 570 and 670 K, in which the overall reaction rate decreases with increasing temperature. Many believe this to be a transition region separating a low temperature reaction regime from that of an intermediate temperature reaction regime. Thus, when considering the oxidation of hydrocarbons below about 1000 K, it should be realized that there are two distinct reaction regimes: low temperature (<650 K) and intermediate temperature (>650 K). It will be shown that the chemistry in each of these reaction regimes is very different.

The oxidation of hydrocarbons in the low temperature regime has been the subject of extensive study in the past. Most of the work has been reviewed by McKay (1977), Pollard (1977), Benson (1976, 1981, 1982), Minkoff and Tipper (1962) and Lewis and Von Elbe (1961). One hydrocarbon which has received much attention is propane (Pease _et al_., 1934, 1938; Newitt and Thornes, 1937; Knox and Norrish, 1954; and Lefebvre and Luquin, 1965). Propane is the simplest fuel which exhibits cool flame and negative temperature coefficient characteristics, yet it is generally representative of higher molecular weight alkanes. This section of the report presents the results of the experimental of the stable hydrocarbon species present in the samples. The samples from the higher molecular weight fuel, dodecane, were separated on a 3.05 m long x 0.3175 cm diameter stainless steel 10% silicone SE-30 on 80/100 mesh Chromosorb W-HP packed column.

Due to the numerous intermediates and products from the oxidation of the dodecane, only semi-qualitative species analysis was obtained. For the propane and propene, however, both detailed qualitative and quantitative species determinations were obtained. The uncertainty in the species measurements for these fuels was ±3% for the alkanes, alkenes and carbon oxides and ±6% for the oxygenated hydrocarbons. Other species which were expected to be present but were not monitored included H_2, O_2, H_2O and H_2O_2. Formaldehyde was detected and analyzed from the propene samples. However, with the propane samples, although formaldehyde formation was expected, it did not appear on the chromatogram. This was attributed to the closeness of the formaldehyde retention time to that of the propane, causing the formaldehyde to be masked by the much larger propane peak.

For each initial condition, experiments were repeated and samples taken at different times during the course of the reaction until enough data were obtained to construct species concentration profiles. Since each GC sample was obtained from a separate run, the reproducibility of the system was very important. With a new reaction vessel, it was found that in addition to washing with nitric acid, several runs were required (20-30 for the gaseous fuels; 40-50 for the liquid fuels) to condition (age) the surface until the data became reproducible. The criteria for reproducibility was that the induction period not vary more than 2%, the maximum temperature not vary more than 1 degree, and the maximum pressure not vary by more than 2 torr. To assure that reproducibility was maintained during each experiment at a given condition, the pressure and temperature histories were carefully monitored up to the time of sample withdrawal.

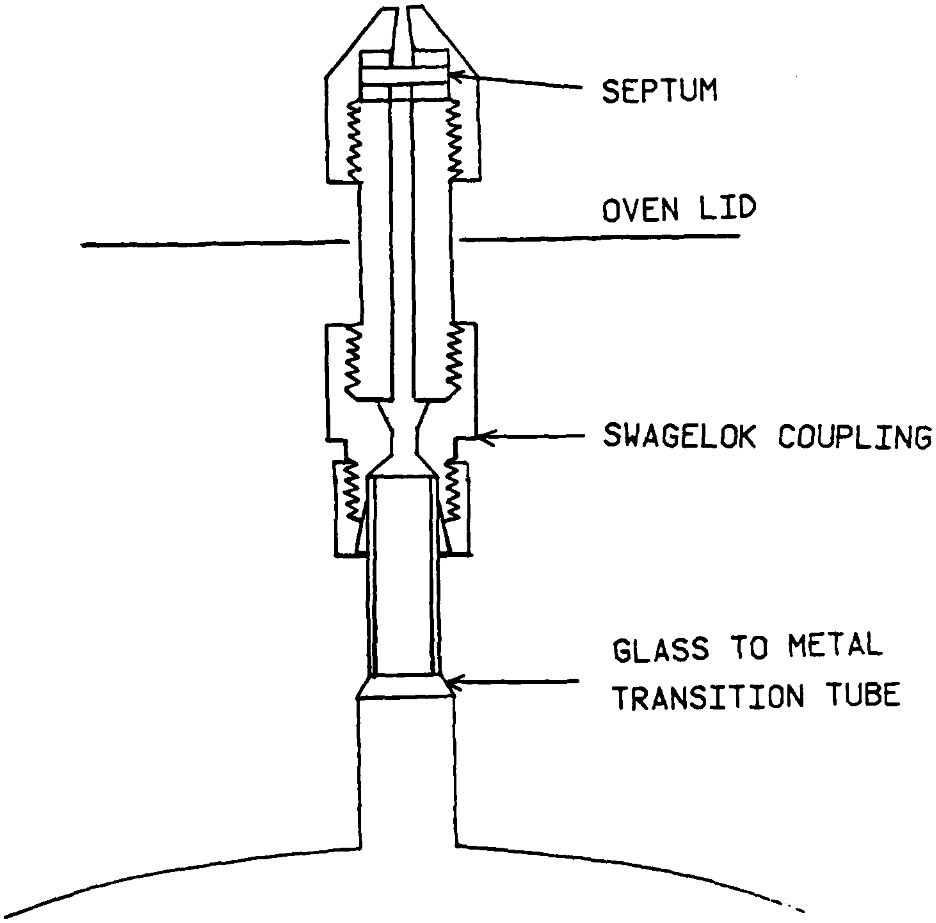


FIG. 2. INJECTOR ASSEMBLY

analysis. This sampling yielded excellent temporal resolution considering the slowness of the reaction (taking on the order of minutes) under the conditions used for this work.

For the experimental work on the liquid fuels, a reaction vessel with the same size and shape as that employed for the gaseous fuels was used. However, a special syringe adapter was attached on this vessel to facilitate the direct injection of liquid fuels. The injector, shown in Fig. 2, is similar to those used in gas chromatographs and consists of a brass body which extended through the lid of the oven. A silicone rubber septum was used to provide a vacuum tight seal. Microliter syringes, equipped with 152 mm long needles, were used to penetrate the length of the injector coupling and inject the fuel directly into the main body of the reaction vessel which was prefilled with the desired amount of oxidizer. Thus, for this work, the premixing apparatus was not used. It is noted that the experimental technique of direct injection of liquid fuels had been used successfully in previous work by Cullis *et al*. (1981) and Reading (1978).

A gas sampling valve was used to inject a portion of the acquired samples (0.25 cm^3) into a Varian 3700 gas chromatograph equipped with a flame ionization detector (FID). The FID was fueled by a mixture of hydrogen (30 cm^3/min) and air (300 cm^3/min). The samples from the low molecular weight gaseous fuels (propane and propene) were separated on a 2.4 m long x 0.3175 cm diameter stainless steel Porapak Q 80/100 mesh packed column. Helium carrier gas (25 cm^3/min) was used for the propane and nitrogen carrier gas (25 cm^3/min) was used for the propene. A nickel catalyst, located downstream of the column, was used to methanize the carbon oxides, facilitating their detection on the FID. Temperature programming (5 min at 36°C; 8°C/min to 160°C) was used to obtain adequate separation of the carbon oxides and most

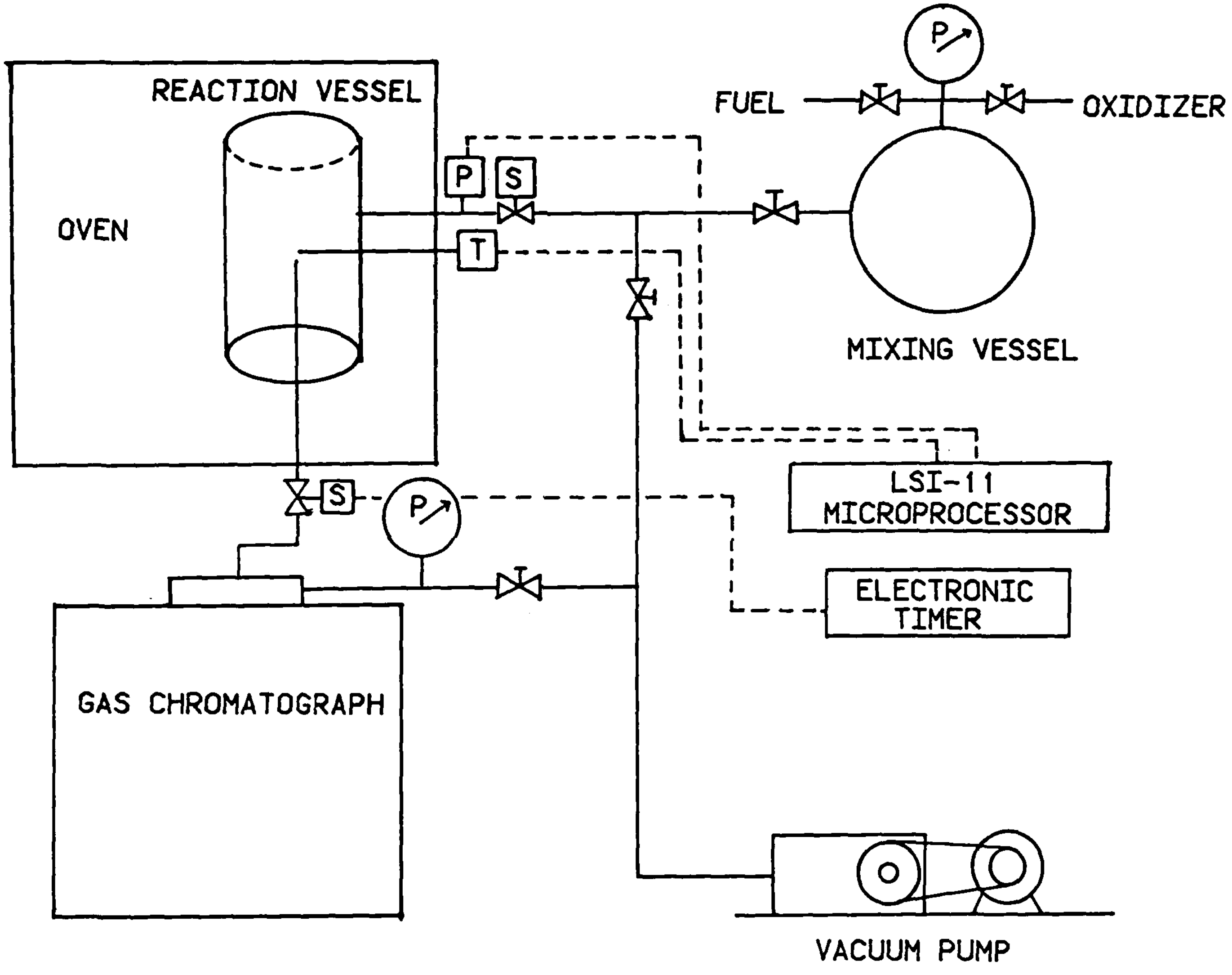


FIG. 1. EXPERIMENTAL FACILITY

II. EXPERIMENTAL FACILITY AND PROCEDURES

The experimental facility, shown in Fig. 1, consists of a cylindrical pyrex reaction vessel (volume 1395 cm^3, diameter 10 cm, surface/volume 0.5 cm^{-1}) located inside a temperature regulated oven. Before use, the inner surface of the vessel was cleaned with nitric acid, rinsed with distilled water and then baked under vacuum at 450°C for 10 hours. The pressure inside the reaction vessel was monitored by a Setra Model 204 pressure transducer installed on a neck of the vessel which extended through the oven wall. The temperature was measured at the center of the vessel with a platinum/platinum-13% rhodium thermocouple constructed of 0.05 mm diameter wires, which were passed through a 1.58 mm alumina insulator. To protect against catalytic heating caused by the platinum wire, the thermocouple was coated with a thin layer of silica.

For the experimental work on the gaseous fuels, a spherical pyrex mixing vessel (volume 2125 cm^3) was used to mix the fuel and oxidizer. The desired mixture ratio of the reactants was obtained on the basis of partial pressures as measured with a Bourdon tube pressure gauge. A homogeneous fuel/oxidizer mixture was achieved primarily by diffusive mixing for 30 minutes. Following the mixing process, the gaseous mixture was rapidly admitted, by way of a solenoid valve through a 0.63 cm line, into the evacuated, preheated reaction vessel. The pressure and temperature data were recorded on a strip chart and stored on floppy disk using an LSI-11 microprocessor. At a selected time during the reaction, the experiment was terminated by withdrawing a portion (20%) of the reacting mixture for detailed analysis. This was accomplished using another solenoid valve leading into an evacuated sampling loop where the reacting gas sample was quenched. The solenoid valve was opened for a duration of 1 second to obtain a sample of adequate size for chromatographic

(9) Wilk, R.D., Cernansky, N.P., and Cohen, R.S., "The Effects of Fuel Structure and Fuel Mixtures on Autoignition," under preparation for Journal submission.

(10) Wilk, R.D., "Preignition Oxidation Characteristics of Hydrocarbon Fuels," Ph.D. Thesis, under preparation (1985).

involved in facilities maintenance and upgrading. Mr. Hamid Sarv (M.S. 1981), Mr. Jairam Agaram (M.S. 1981) and various undergraduate students were involved early in the development of the experimental and analytical capabilities.

E. REPORTS AND PUBLICATIONS

In addition to the interim progress reports and this final report, work conducted as part of this research program have resulted in the following publications, papers, and presentations.

(1) Sarv, H., "A Protocol for the Analysis of Chromatographic Data with Special Applications in Combustion," Department of Mechanical Engineering Report, Drexel University, Philadelphia, PA, March 1981.

(2) Wilk, R.D., Cohen, R.S. and Cernansky, N.P., "An Experimental Technique to Study the Preignition Oxidation Behavior of Hydrocarbon Fuels," Paper no. WSSCI 82-90, presented at the Fall Meeting of the Western States Section/The Combustion Institute, Livermore, CA, 11-12 October 1982.

(3) Wilk, R.D., Cohen, R.S., and Cernansky, N.P., "The Oxidation of Propane Between 400-500C," Paper no. WSSCI 84-40, presented at the Spring Meeting of the Western States Section/The Combustion Institute, Boulder, CO, 2-3 April 1984.

(4) Wilk, R.D., Cohen, R.S., and Cernansky, N.P., "Low Temperature Oxidation of Propene," Paper no. 84-95, presented at the Fall Meeting of the Western States Section/The Combustion Institute, Palo Alto, CA, 22-23 October 1984.

(5) Wilk, R.D., Cohen, R.S., and Cernansky, N.P., "Ignition Studies of Dodecane and Binary Mixtures of Dodecane and Tetralin," Twentieth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1985.

(6) Wilk, R.D., Cernansky, N.P., and Cohen, R.S., "Low Temperature Oxidation of Propane," Department of Mechanical Engineering Report, Drexel University, Philadelphia, PA, March 1985. Submitted for publication.

(7) Wilk, R.D., Cernansky, N.P., Pitz, W.J., and Westbrook, C.K., "Chemical Kinetics Modeling of the Low Temperature Oxidation and Ignition of Propane and Propene," under preparation, 1985.

(8) Wilk, R.D., Cernansky, N.P., and Cohen, R.S., "Transition in the Oxidation Chemistry of Propane from Low to Intermediate Temperatures," under preparation for Journal submission.

(2) The oxidation chemistry in the intermediate temperature regime should be investigated thoroughly. The static reactor studies are limited to temperatures up to about 750 K. Flow reactor studies should fill the void from 750 to 1000 K.

(3) The effects of pressure on the oxidation chemistry should be determined. Due to experimental constraints, the results from the work described in this report were limited to subatmospheric pressures. Results are desirable at pressures in the range 20-30 atmospheres, which are characteristic of actual combustion systems.

(4) Additional studies are needed on the effects of binary and ternary mixtures of higher molecular weight pure fuels which are representative of the various classes of components in full-boiling range fuels. Results from such studies would be extremely useful in view of the current results showing a complex interaction among the components of a mixture and how they affect the ignition process.

D. RESEARCH PERSONNEL AND ACTIVITIES

The research project was coordinated under the supervision of Professors Nicholas P. Cernansky and Richard S. Cohen as co-principal investigators. They had overall responsibility for conducting, directing, and reporting the various phases of the research program. However, the primary responsibility for carrying out and implementing the details of the experimental and analytical aspects of the program fell on the other technical personnel supported by the project. Mr. Richard D. Wilk (Ph.D. candidate) had the primary responsibility for static reactor operation, sample collection and analysis, and data interpretation. Ms. Patricia Partridge (Ph.D. applicant) was primarily responsible for development of the GC protocols and for maintaining the analytical system. Mr. Robert Tidona (Research Engineer) was

Another aspect of this research project involved the investigation of the preignition behavior of dodecane and binary mixtures of dodecane and tetralin. The cool flame ignition characteristics of dodecane in air were studied at temperatures in the range 523-623 K and at equivalence ratios ranging from 0.5 to 1.0. The effects of the initial temperature, pressure, and equivalence ratio on the induction period were determined. The results from these studies showed that the cool flame behavior of dodecane was consistent with that found for lower molecular weight alkanes. However, unlike the chemistry of the lower alkanes, the acceleration path of the oxidation of dodecane proceeds primarily by the alkylperoxy isomerization route. The effects of adding the aromatic component tetralin were also examined. The addition of the tetralin had the overall effect of decreasing the ignitability, although the magnitude of this effect was not proportional to the amount of the aromatic added. Although no detailed chemical analyses were made on these fuels, the chromatographic peak profiling technique together with results of Fish (1968) and Santoro and Glassman (1979) were applied in order to determine the initial stages of the dodecane oxidation process and the chemical effects of the added tetralin.

C. RECOMMENDATIONS FOR FUTURE WORK

Based on the results and accomplishments of the present work, a number of additional studies are indicated in order to extend our current understanding of hydrocarbon oxidation and ignition processes. In particular:

(1) The low and intermediate temperature detailed preignition chemistry work should be extended to higher molecular weight fuels such as n-butane, isobutane, butene, and isobutene. Little is known about the intermediate reaction paths of these species in the low and intermediate temperature regimes.

from a low temperature regime to an intermediate temperature regime, separated by a region of negative temperature coefficient. The main characteristics and features of the oxidation mechanisms were determined for each fuel in each temperature regime.

In the low temperature regime alkylperoxy and allylperoxy radicals are formed and become the dominant radical species. These can react in several ways, the most important of which leads to the formation of hydroperoxides. Hydroperoxides were determined to be the main chain branching intermediates responsible for the acceleration of the reaction and for the formation of cool flames. In the intermediate temperature regime hydroperoxyl radicals are dominant and lead to hydrogen peroxide, which is the main branching intermediate in this temperature range. These conclusions are based in large measure upon the hydrocarbon products formed which consist mainly of oxygenated species at the lower temperatures and lower alkanes and alkenes at the intermediate temperatures.

Chemical kinetic modeling studies were made in collaboration with Westbrook and Pitz from Lawrence Livermore National Laboratory. The experimental results for propene were used to modify and extend to low and intermediate temperatures their propene reaction mechanism which was originally developed for high temperatures.

Experiments were also performed to determine the effects of reaction vessel surface-to-volume ratio on the oxidation chemistry. The effect of increasing the vessel surface-to-volume ratio was to enhance heterogeneous termination, resulting in longer reaction times. Comparison of the reaction products from vessels with different surface-to-volume ratios showed there to be no significant effect of surface on the main reaction paths of the mechanism.

weight hydrocarbons (Cullis et al., 1973, 1977, 1982; and Kadota et al., 1976) and on actual fuels (Spadaccini and TeVelde, 1982). In addition, there have been some studies made of the ignition characterisitcs of binary hydrocarbon mixtures. Salooja (1968) reported on the ignition behavior of a number of binary mixtures composed of both aliphatic and aromatic components in the C_6-C_8 range. Cullis and Foster (1974) and Brezinsky and Dryer (1985) also studied the effects on the oxidation and ignition of mixtures of branched and straight chain hydrocarbons. More work is needed on fuel mixtures, though, especially mixtures of different fuel classes such as alkanes and aromatics and straight and branched chain alkanes.

The research project reported herein involved studies of the preignition oxidation characteristics of selected hydrocarbons. It was undertaken with the purpose of supplementing and extending the previously mentioned work by examining new reaction regimes of previously studied fuels and by studying higher molecular weight fuels and their mixtures.

B. PROJECT SUMMARY

As noted, this project was directed towards the study of the preignition oxidation characteristics of hydrocarbon fuels. It involved detailed studies of the oxidation chemistry of propane and propene, as well as studies of the general ignition characteristics of dodecane and binary mixtures of dodecane and tetralin.

Comprehensive studies were made of the oxidation of propane and propene at low and intermediate temperatures (550-750 K) in a static reactor system. Studies were made at subatmospheric pressures and at equivalence ratios ranging from 0.8 to 4.0. Stable reaction intermediate and product species were quantified using gas chromatography. The experimental results for each of these fuels demonstrated a clear transition in the oxidation chemistry

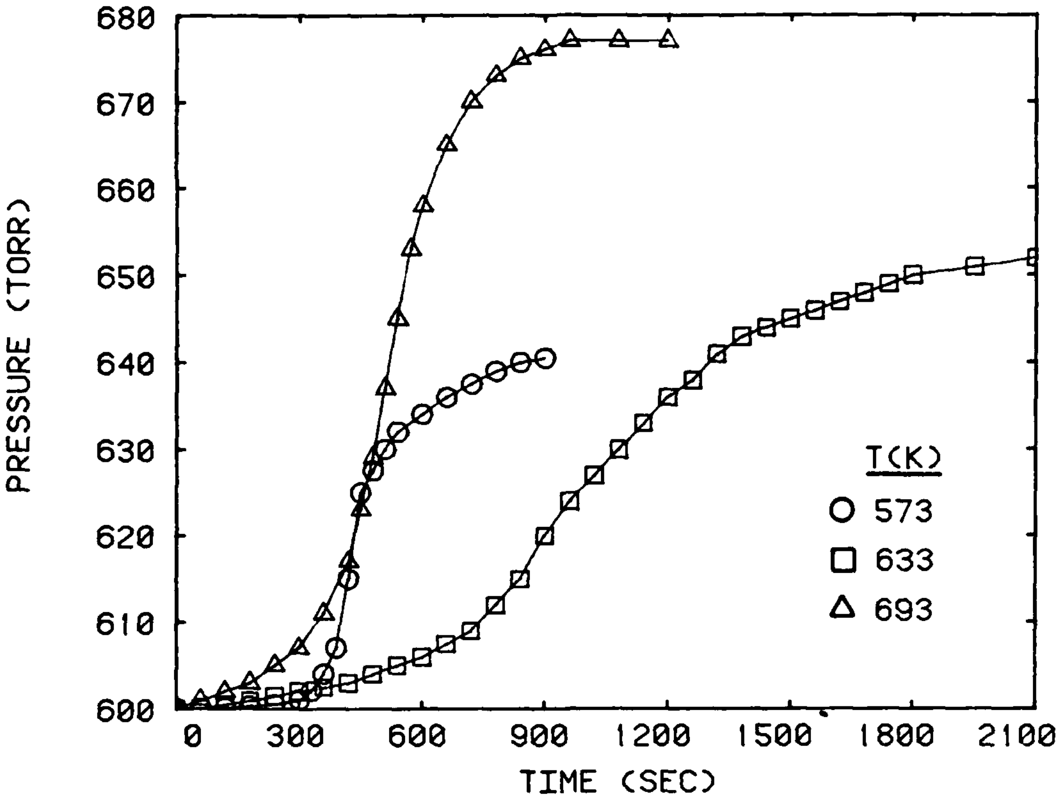


FIG. 3. EFFECT OF INITIAL TEMPERATURE ON THE PRESSURE HISTORIES FOR C_3H_8/AIR MIXTURES AT Φ=2.0.

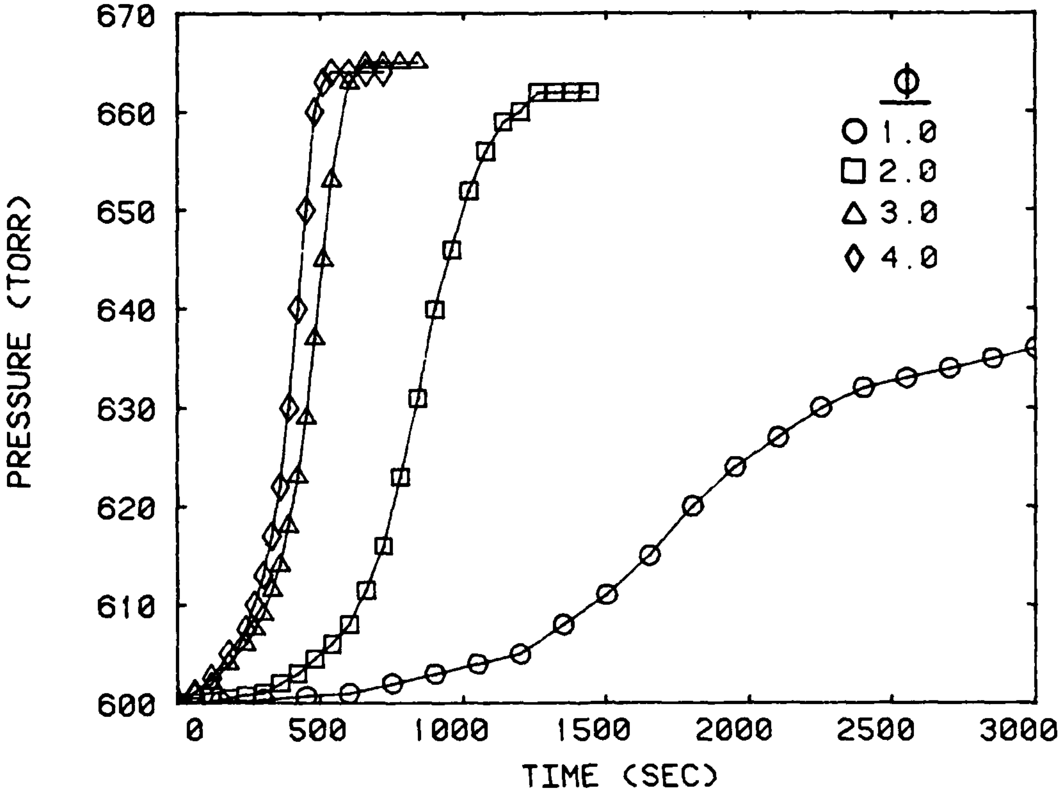


FIG 4. EFFECT OF EQUIVALENCE RATIO ON THE PRESSURE HISTORIES FOR C_3H_8/AIR MIXTURES AT To=673 K.

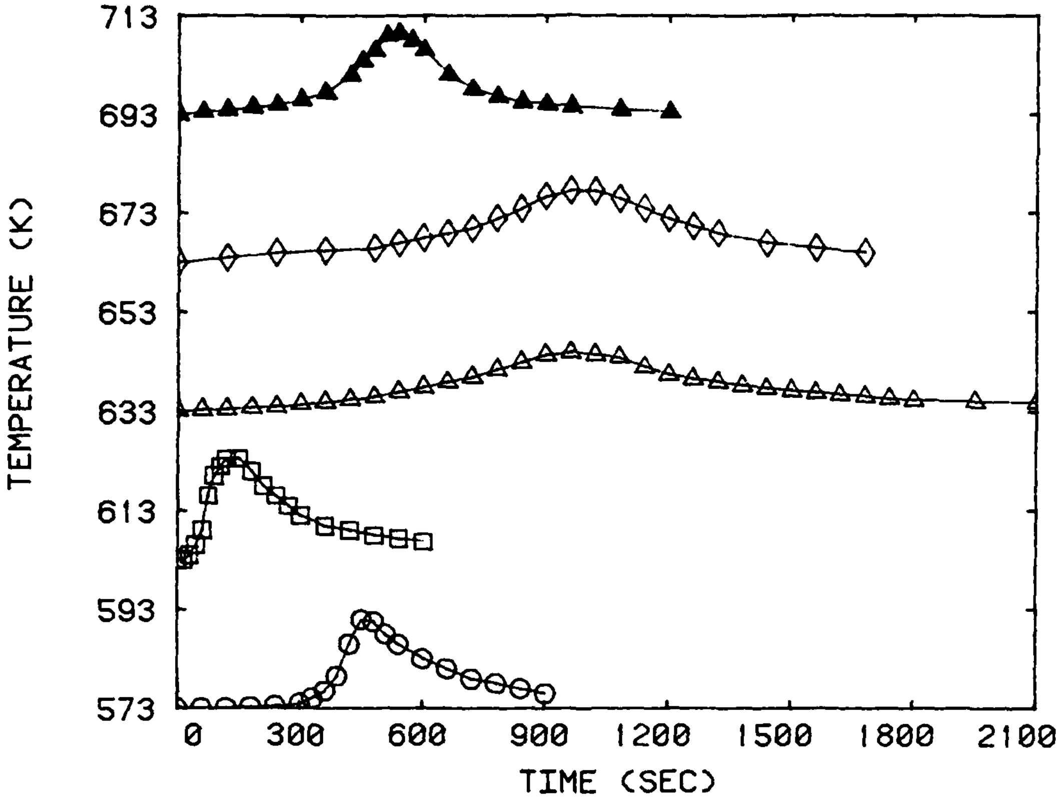


FIG. 5. EFFECT OF INITIAL TEMPERATURE ON THE TEMPERATURE HISTORIES FOR C_3H_8/AIR MIXTURES AT Φ=2.0; P_o=600 TORR.

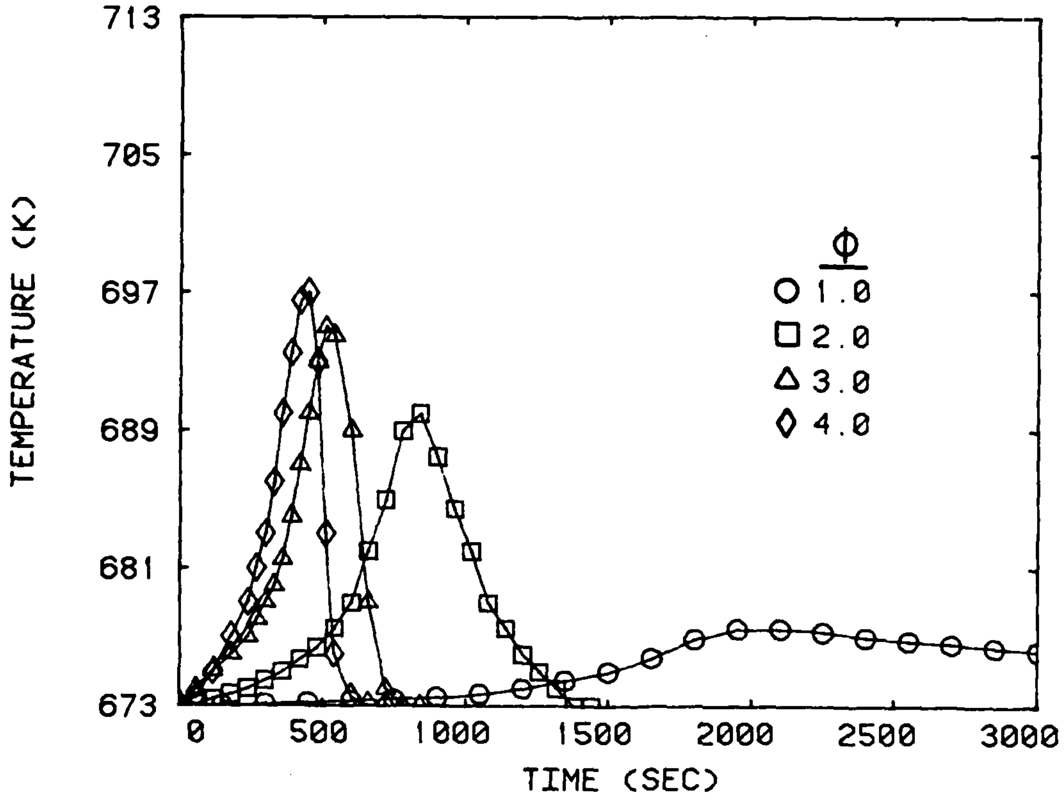


FIG. 6. EFFECT OF EQUIVALENCE RATIO ON THE TEMPERATURE HISTORIES FOR C_3H_8/AIR MIXTURES AT P_o=600 TORR.

rate begins to slow again.

The initial temperature has an interesting effect on the induction period (Fig. 7) and on the maximum rate of pressure rise (Fig. 8). As the initial temperature is increased up to about 600 K, the induction period decreases and the maximum rate increases. However, in the temperature range from about 600-650 K, further increase in temperature results in an increase in the induction period and a decrease in the maximum rate. Finally, above 650 K, the induction period again decreases with a corresponding increase in the maximum rate. This behavior is attributed to the negative temperature coefficient (NTC) phenomenon associated with hydrocarbon oxidation. This phenomenon has been reviewed by Dechaux (1973). The region of NTC obtained in the current study, 600-650 K, is in good agreement with previous results obtained from earlier studies on propane by Pease (1938) (600-650 K), Seakins (1961) (600-660 K), Mulcahy (1947) (593-633 K), and Nguyen *et al.* (1970) (623-658 K).

The temperature range at which the NTC behavior occurs represents a transition in the oxidation chemistry from a low temperature mechanism, in which cool flames and two-stage ignition can occur, to an intermediate temperature mechanism which can lead to single-stage ignition. At temperatures in the range 563-600 K, below the NTC range, the occurrence of cool flames was indicated by sharp pressure pulses superimposed on the normal pressure-time curves (Fig. 9), as well as by thermal pulses on the temperature profiles (Fig. 10). These pulses were predominantly for fuel rich mixtures (ϕ>1.0), and at the richest conditions examined (ϕ=3.0, 4.0) multiple oscillations were observed. Increasing the propane concentration in the mixture increased both the number and intensity of the cool flames (Fig. 11). The occurrence of the cool flames produced pressure rises up to 60 torr and temperature rises up to 40 degrees.

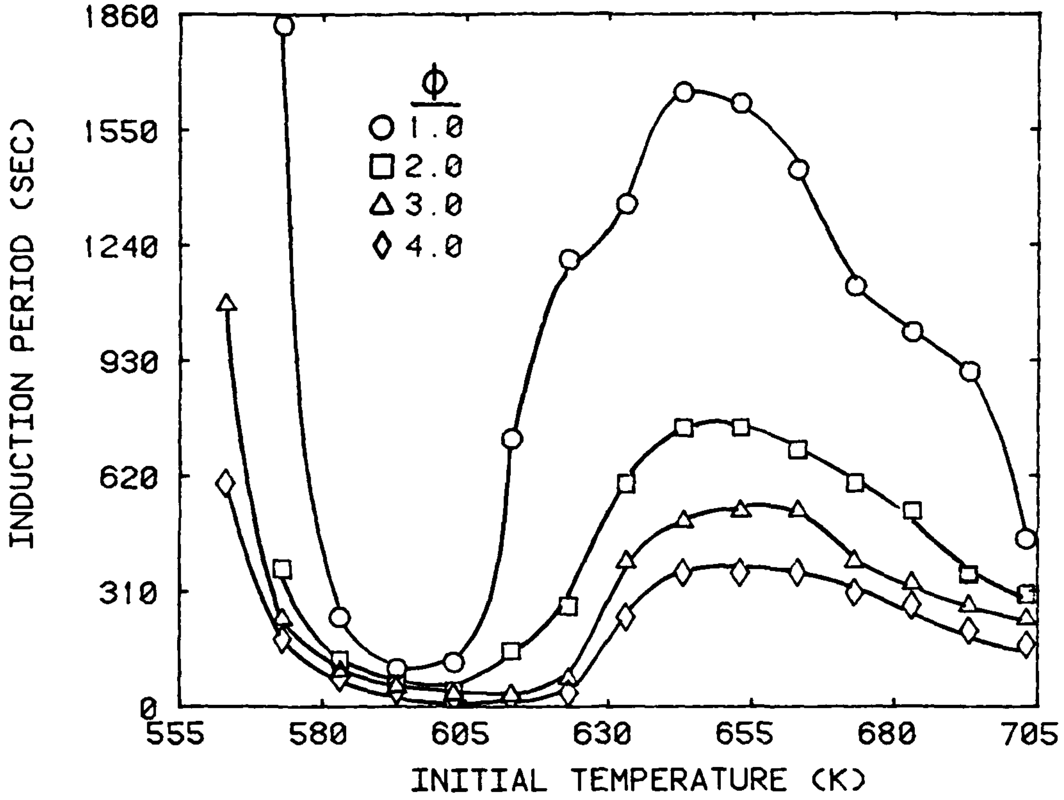


FIG. 7. EFFECT OF INITIAL TEMPERATURE AND EQUIVALENCE RATIO ON THE INDUCTION PERIOD. Po=600 TORR.

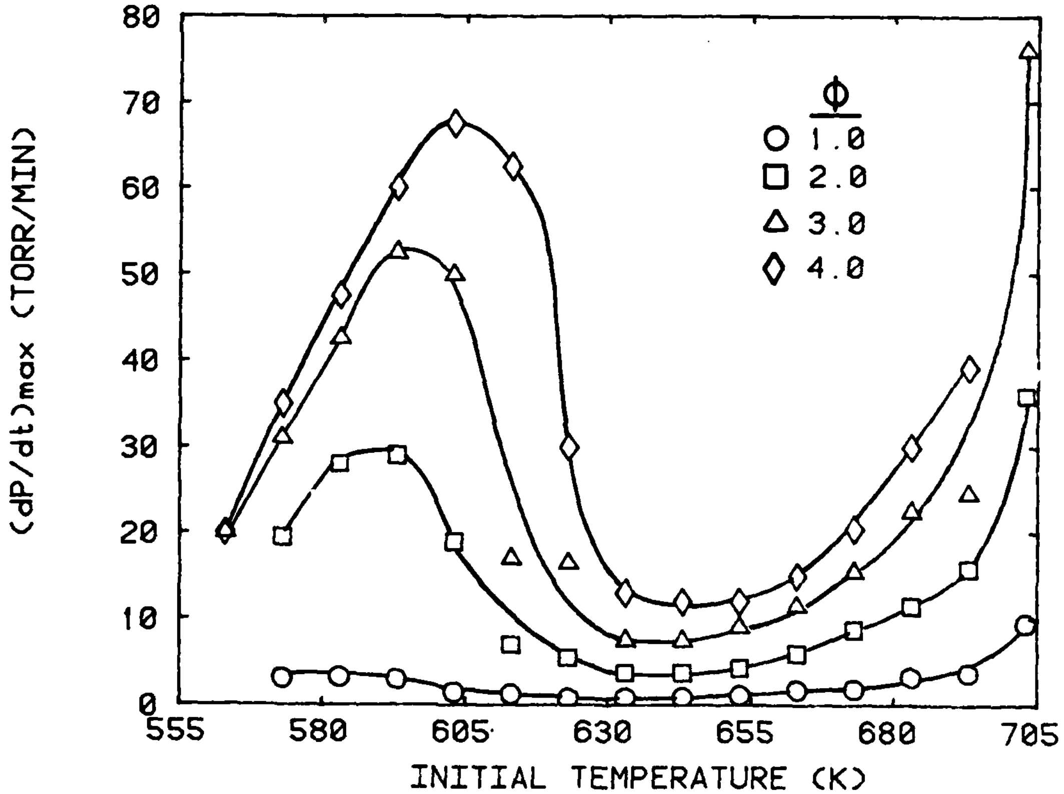


FIG. 8. EFFECT OF INITIAL TEMPERATURE AND EQUIVALENCE RATIO ON THE MAXIMUM RATE OF PRESSURE RISE.

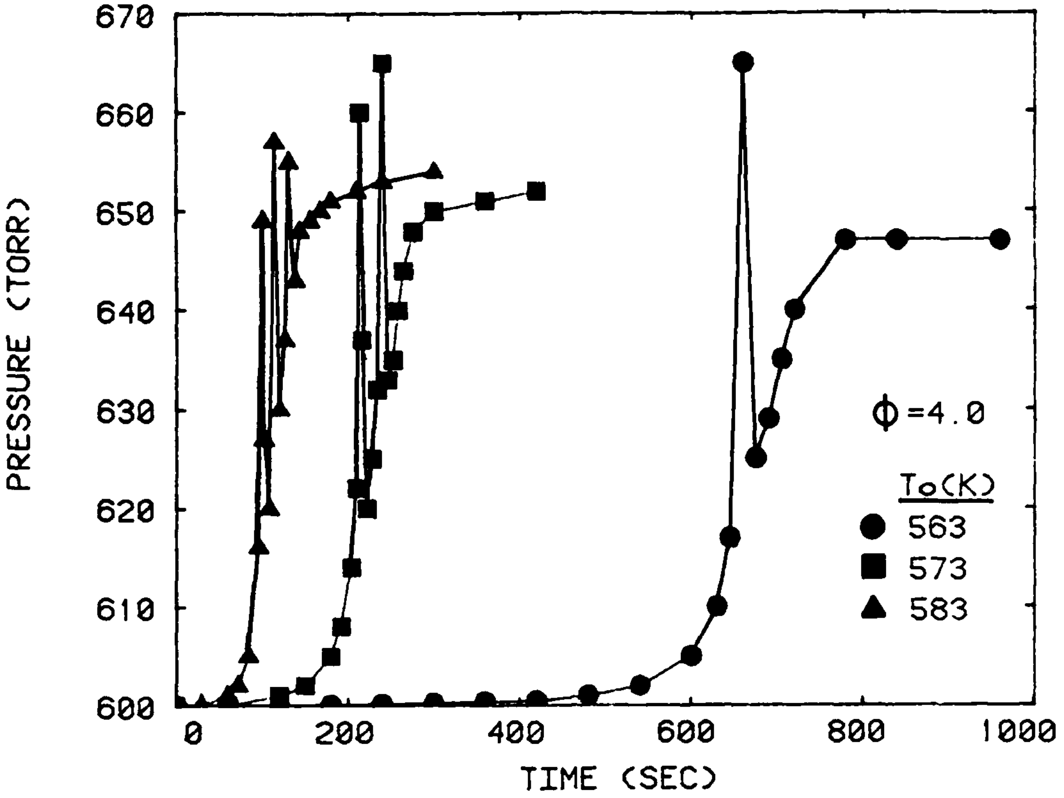


FIG. 9. EFFECT OF INITIAL TEMPERATURE ON THE PRESSURE HISTORIES AND COOL FLAMES FOR C_3H_8/AIR MIXTURES.

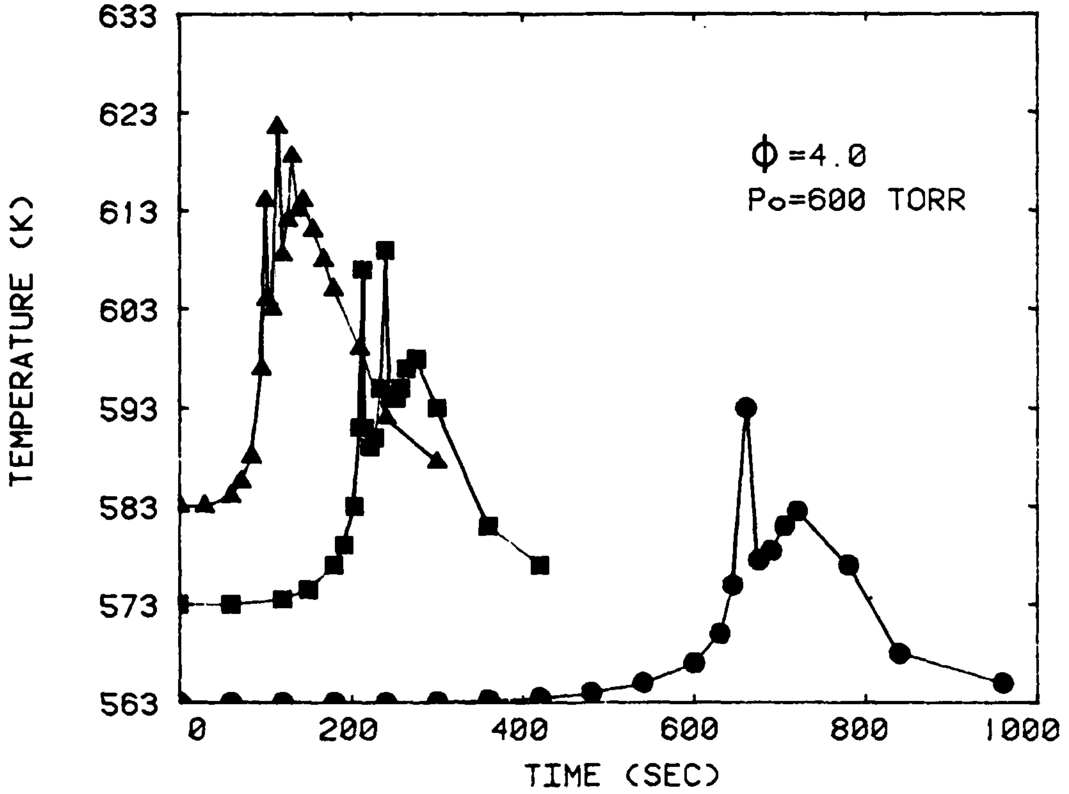


FIG. 10. EFFECT OF INITIAL TEMPERATURE ON THE TEMPERATURE HISTORIES AND COOL FLAMES FOR C_3H_8/AIR MIXTURES.

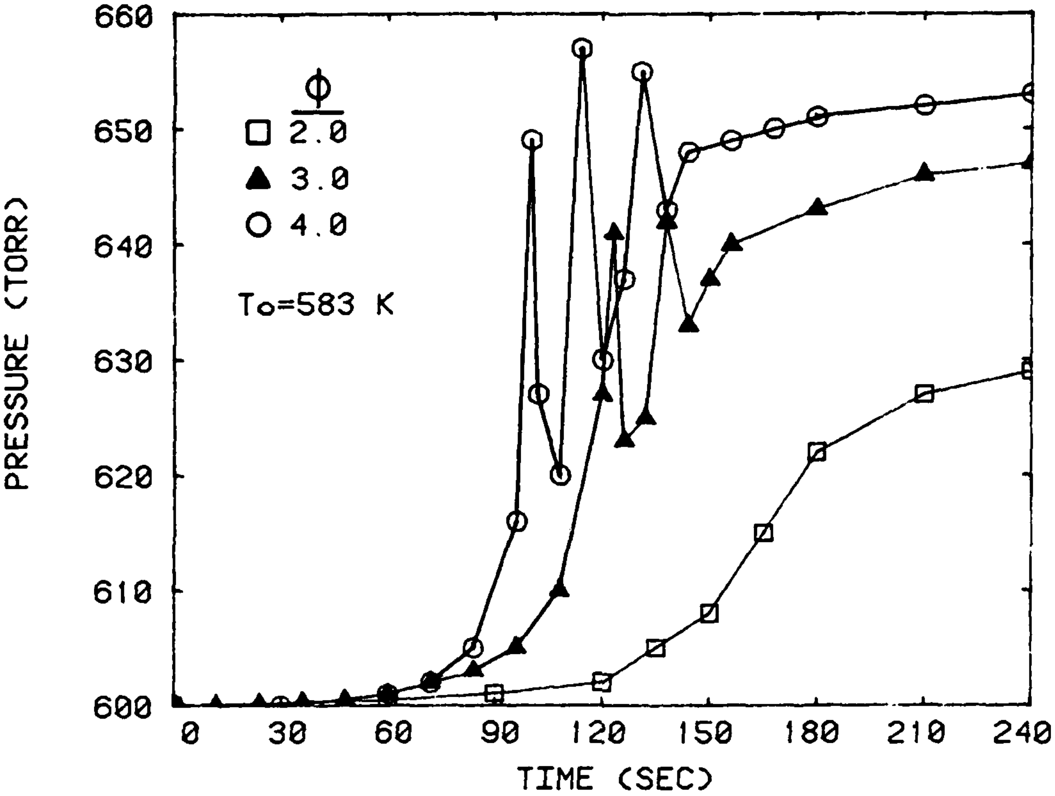


FIG. 11. EFFECT OF THE EQUIVALENCE RATIO ON THE PRESSURE HISTORIES AND COOL FLAMES FOR C_3H_8/AIR MIXTURES.

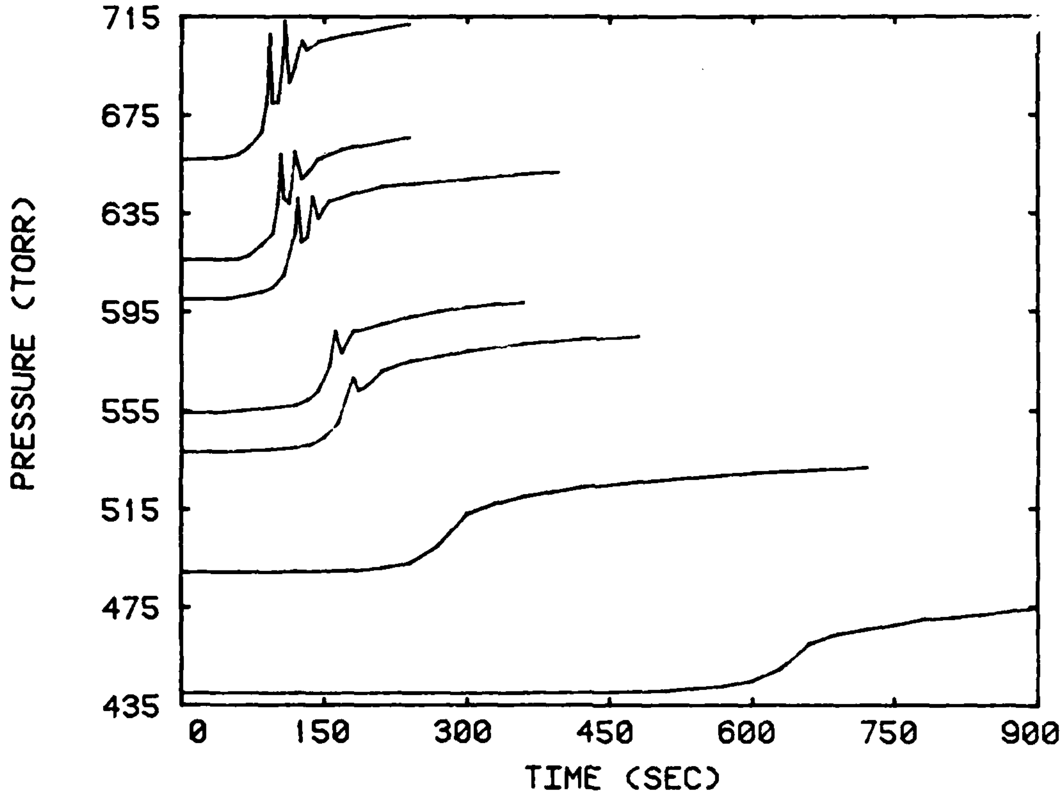


FIG. 12. EFFECT OF INITIAL PRESSURE ON THE PRESSURE HISTORIES FOR C_3H_8/AIR MIXTURES AT $\Phi=3.0$; To=583 K.

The cool flame phenomenon is related to the negative temperature coefficient and the associated change in mechanism. Cool flames form when the branching intermediate builds up to a critical concentration, increasing the rate of chain branching and thus increasing the temperature, pressure, and overall reaction rate. As the temperature increases, a shift in mechanism occurs as competing reactions inhibit the formation of the branching agent. Chain branching by the main mechanism ceases, causing a corresponding decrease in temperature, pressure, and reaction rate. Thus, the process is self-inhibiting. Under certain conditions, as seen from the experimental results, the process can repeat itself and lead to multiple oscillations. Also, in some cases (higher pressures, richer mixtures), two-stage ignition can occur where the cool flame conditions the mixture in such a way that a hot ignition can follow.

It is often useful to characterize the intermediate and low temperature regimes by obtaining an overall apparent activation energy for each. The dependence of some characteristic time of the reaction on the initial temperature can be represented by an equation of the form:

$$\tau_{mr} = A \exp(Ea/RT_o)$$

where, in this case, the characteristic time used (τ_{mr}) was that employed by Nguyen <u>et al</u>. (1970) and is equal to the time from admission of the reactants to the attainment of the maximum rate. E_a is the apparent overall activation energy, A is a preexponential constant and T_o is the initial absolute temperature. This correlation was applied to the data in each of the reaction regimes. Values of E_a were obtained and are presented in Table I, along with values obtained by Nguyen <u>et al</u>. (1970). As can be seen from the table, the values of E_a from the two studies are in good agreement, differing by a maximum of 6%, which is well within the experimental error.

TABLE I. Comparison of Overall Activation Energies for Low and Intermediate Temperature Propane Oxidation

	Ea (kcal/mol) (current study)	Ea (kcal/mol) (Nguyen et al., 1970)
Low Temperature (T<600 K)	53	50
Intermediate Temperature (T>670 K)	25	24

The effect of varying the initial pressure on the reaction can be seen by examining Fig. 12, which shows several pressure-time traces obtained at an equivalence ratio of 3.0, and initial temperature of 583 K. In general the induction period is very sensitive to small changes in pressure, decreasing from 600 to 72 seconds as the initial pressure increased from 440 to 657 torr. Cool flames began to appear as the pressure increased, as indicated by the pressure pulses, and the number and intensity of the cool flames increased with initial pressure.

2. Species Measurements

Results from the analytical species measurements are shown in Figs. 13 and 14, and are presented in the form of species concentration profiles. The actual data points are shown along with the smoothed curves. Carbon monoxide was found to be the major product of oxidation. This was the case even at lean and stoichiometric conditions. Other major products that were measured included carbon dioxide, ethene, methane, acetaldehyde (ethanal), methanol and propene. Methanol was the major hydrocarbon species formed at the lower temperature, while propene was the major hydrocarbon species formed at the higher temperatures. Propene oxide and propionaldehyde (propanal) were also present and are given as a single combined quantity since they could not be

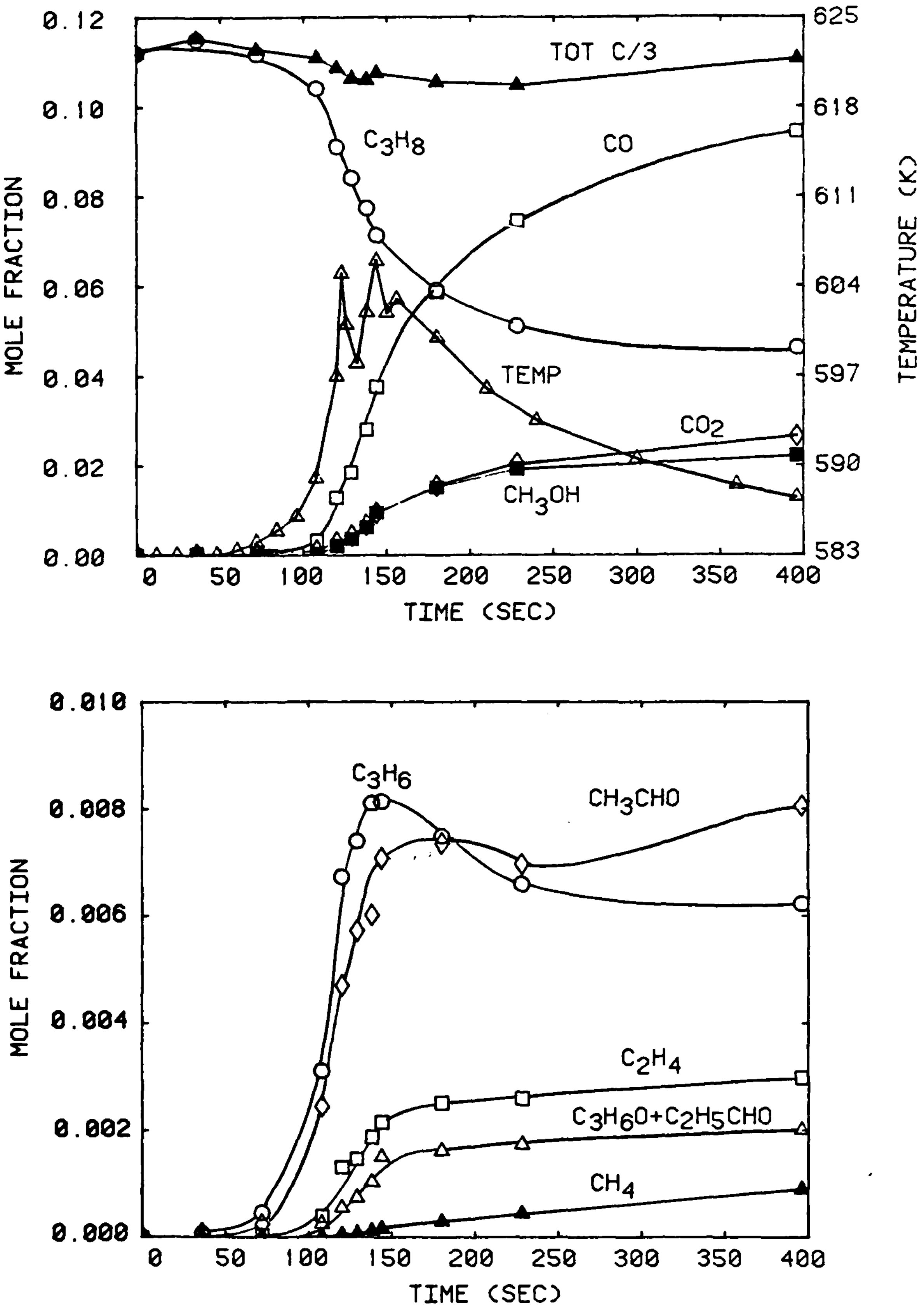


FIG. 13. SPECIES CONCENTRATION AND TEMPERATURE PROFILES FOR C_3H_8/AIR MIXTURES AT $\phi=3.0$; Po=600 TORR; To=583 K.

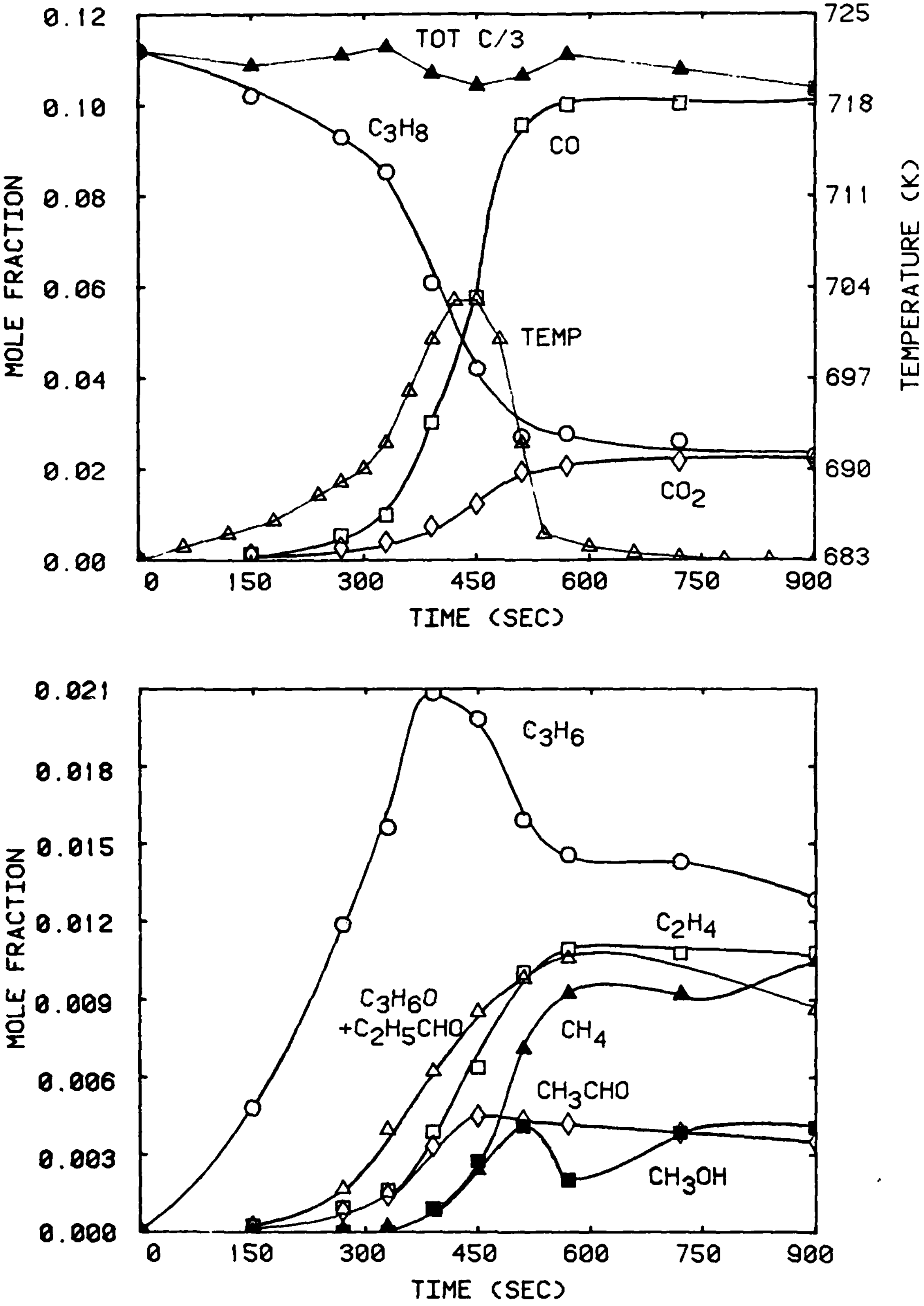


FIG. 14. SPECIES CONCENTRATION AND TEMPERATURE PROFILES
FOR C_3H_8/AIR MIXTURES AT $\phi=3.0$; Po=600 TORR; To=683 K.

separated individually by the gas chromatograph at all conditions. However, from the conditions at which separation was achieved, it was found that the majority component was propene oxide, comprising about 70% of the total combined quantity for the case at 583 K and about 88% for the case at 683 K. There were some minor products measured as well. At 583 K, these included ethane, acetone, and isobutane, each with a maximum concentration less than 0.08%. At 683 K, these same minor products were measured, each with a maximum concentration less than 0.16%. Other minor products observed at this temperature included n-butane, n-butene, isobutene, and 1,3-butadiene, all with maximum concentrations less than 0.1%.

The propane disappearance profiles, as well as the concentration profiles of many of the products, display the same sigmoidal shape as the pressure profiles, starting out slow, accelerating to a maximum and then slowing again. Many of the products formed in the early stages of the reaction, such as propene and acetaldehyde, are readily oxidized and can become the source of secondary oxidation products. Therefore, the species concentration profiles shown represent the net concentrations as the species are being produced and consumed simultaneously.

It can be seen that there are significant differences in the reaction products as the initial temperature is increased from 583 K in the lower temperature regime (Fig. 13) to 683 K in the intermediate temperatures regime (Fig. 14). The amount of propane consumed increases with temperature from about 59% at 583 K to about 80% at 683 K. There is also a shift from the production of oxygenated hydrocarbon species at the lower temperatures to the production of alkanes and alkenes at the higher temperatures. For example, the maximum net yield of acetaldehyde decreases by about 44% and that of methanol decreases by about 82% as the temperature is increased from 583 K to 683 K.

On the other hand, the maximum net yield of propene increases by 157%, that of ethene by 275% and that of methane by a dramatic 1200%. An exception to this trend is with propene oxide, the concentration of which increases by about 400% instead of decreasing with temperature as do the other oxygenates. Finally, the net yields of the carbon oxides show relatively little change with temperature.

Two cool flames were indicated at 583 K, $\phi=3.0$, as can be seen from the pulses on the temperature profile in Fig. 13. These occurrences seemed to have little effect on the corresponding species profiles as there were no abrupt changes in the net yields of any of the species during the pulses.

Additional species measurements were made in the intermediate temperature regime, this time at lean and stoichiometric conditions ($\phi=0.8$, 1.0). These results are presented in Figs. 15-18. It can be seen from Figs. 15 and 16 that increasing the initial temperature in this intermediate temperature regime rapidly accelerates the reaction. In addition, it can be seen that the relative yield of CO begins to decrease while that of the CO_2 begins to increase. This implies that the temperature is sufficiently high to initiate some conversion of CO to CO_2. Finally, at 743 K, $\phi=1.0$ (Fig. 17), a hot ignition occurred. This was accompanied by a sharp rise in pressure and temperature. Also, there was a sudden decrease in the concentrations of CO and all hydrocarbon species and a corresponding increase in the concentration of CO_2. At the same initial temperature but at $\phi=0.8$ (Fig. 18), the reaction did not accelerate to hot ignition but behaved as the other intermediate temperature cases.

3. Surface Effects

The effect of increased vessel surface-to-volume ratio was examined. An experiment was performed in a higher S/V reaction vessel under the same

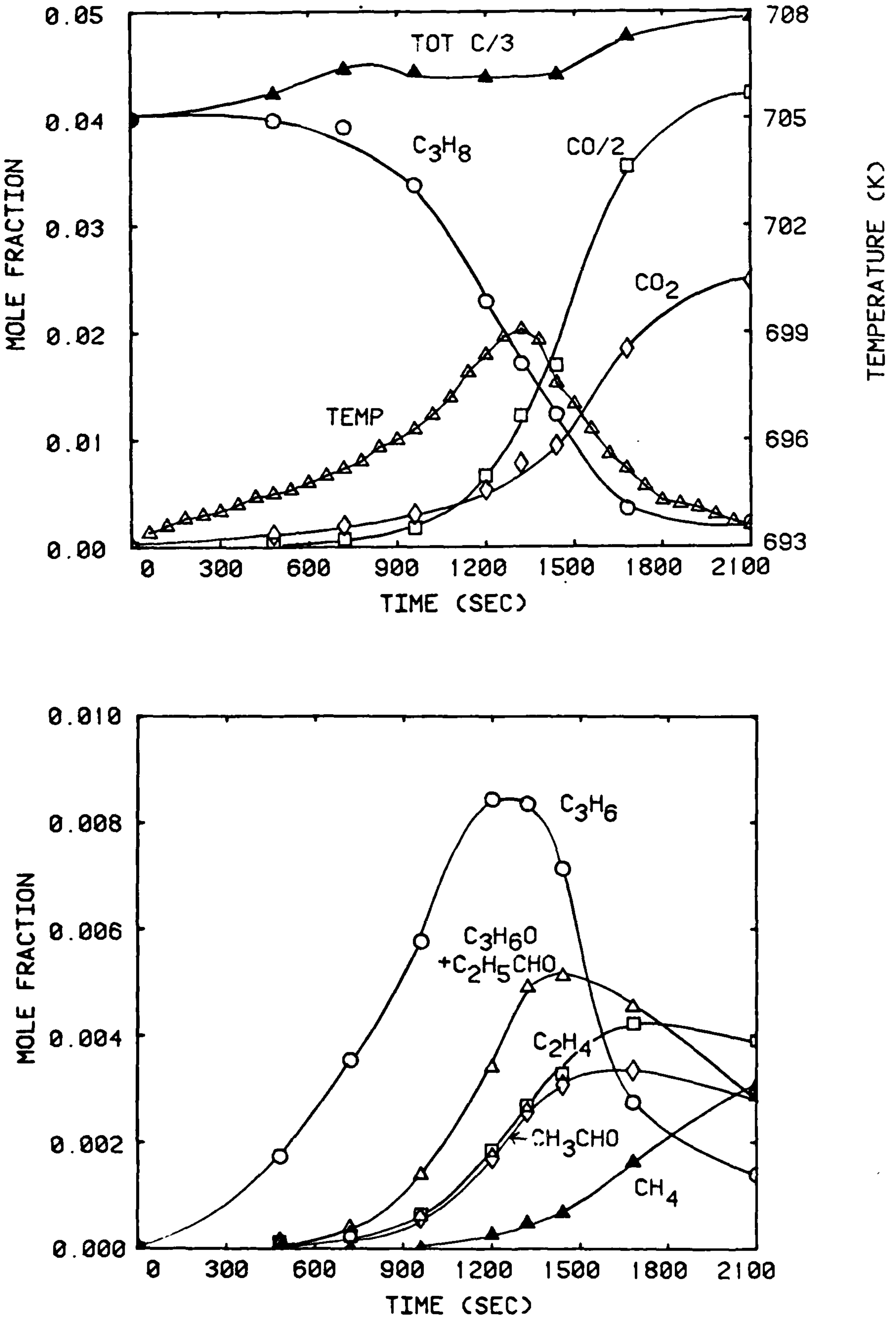
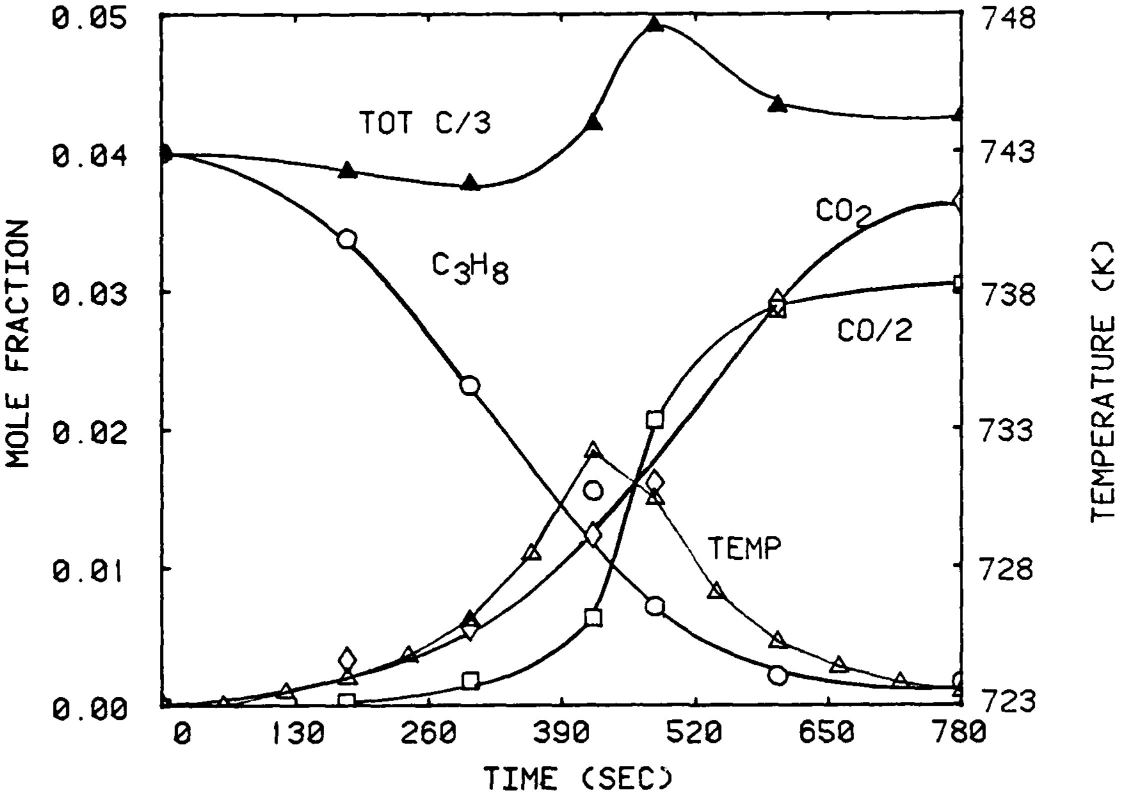


FIG. 15. SPECIES CONCENTRATION AND TEMPERATURE PROFILES FOR C_3H_8/AIR MIXTURES AT ϕ=1.0; Po=600 TORR; To=693 K.



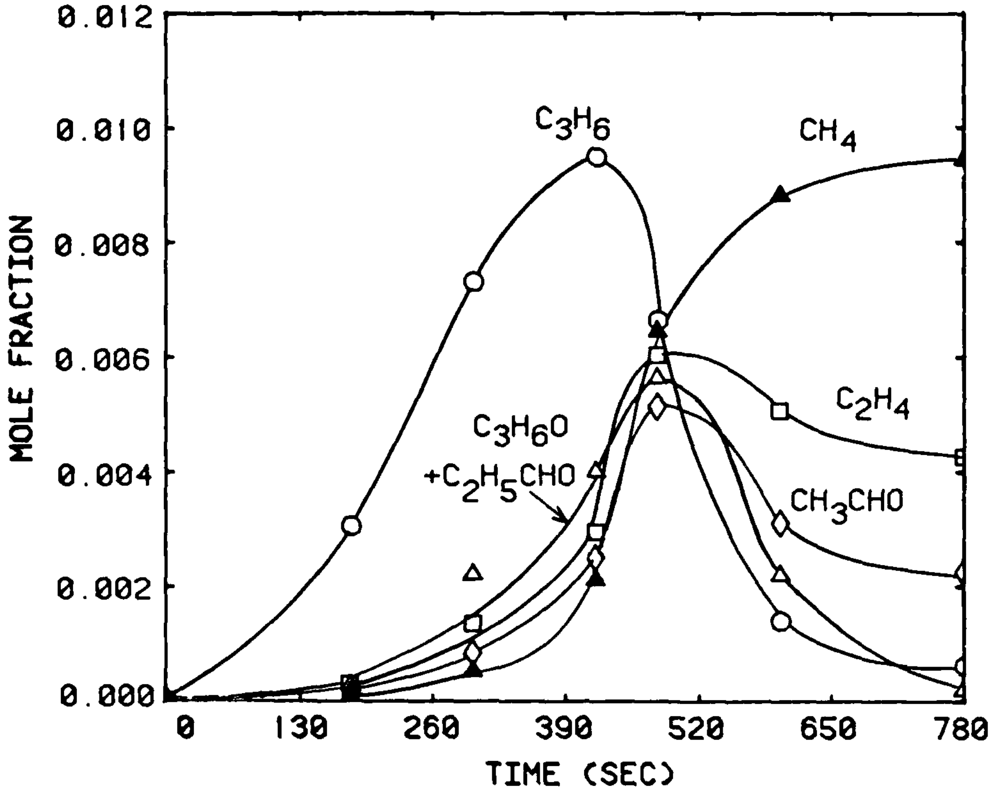


FIG. 16. SPECIES CONCENTRATION AND TEMPERATURE PROFILES FOR C_3H_8/AIR MIXTURES AT $\phi=1.0$; Po=600 TORR; To=723 K.

5. Cool Flames, NTC and Mechanism Transition

Since it was concluded that ROOH is the main branching agent at the lower temperatures, it is necessary to relate what is happening from the chemistry standpoint, involving the ROOH, and what is observed physically such as cool flames and the negative temperature coefficient regime.

Cool flames result from a build-up of ROOH which rapidly decomposes into RO and OH. This branches the chain and greatly accelerates the reaction, producing a rapid rise in temperature and pressure. However, as the temperature increases, the accelerating mechanism is effectively turned off as the ROOH production drops. The amount of ROOH produced is determined by the amount of RO_2 available. As the temperature increases, the production of ROOH decreases due to the overall decrease in the formation of RO_2 (competition between Reactions 5 and 6) and also to the increased importance of alternative reactions (isomerization, decomposition) of the RO_2. During a cool flame pulse then, the rapid acceleration of the reaction cannot be sustained as the ROOH is consumed faster than it is produced. The reaction rate decreases with a corresponding decrease in temperature and pressure. But as the temperature decreases, the rapid branching mechanism may be switched back on as the production of ROOH becomes important again. This could lead to further cool flame oscillations. If the conditions allow, multiple cool flames are possible. As many as four cool flames were observed in these propane experiments.

It would be expected that the cool flame region should be adjacent to the region of NTC. This was found to be the case experimentally. The cool flame region extended from about 563 K to about 593 K, while the region of NTC began at about 600 K, as determined from the plots of induction period and maximum rate against temperature.

The transition from the reactive low temperature zone to the relatively be used to explain the variety of reaction intermediates and products formed at the lower temperatures. As already shown, the RO_2 can decompose unimolecularly to form oxygenated species such as aldehydes. It can also abstract a hydrogen from another source to form a hydroperoxide. It has been determined by Fish (1964, 1968) that another alternative path for the RO_2 is important and should be considered. This route involves the isomerization of the alkylperoxy radical by intramolecular hydrogen transfer from a carbon to the outer oxygen of the peroxy group, forming a hydroperoxyalkyl radical:

$$RO_2 \rightarrow QOOH \qquad (20)$$

This radical can then decompose to an oxiran and a reactive OH radical:

$$QOOH \rightarrow \underset{\text{(oxiran)}}{QO} + OH \qquad (21)$$

or it can react further with oxygen to eventually form a dihydroperoxide which can then break apart and branch the chain. Benson (1981) presented this scheme for propane:

$$C_3H_7O_2 \rightarrow C_3H_6OOH \qquad (22)$$

$$C_3H_6OOH \rightarrow C_3H_6O + OH \qquad (23)$$

$$C_3H_6OOH + O_2 \rightarrow O_2C_3H_6OOH \qquad (24)$$

$$O_2C_3H_6OOH \rightarrow HO_2C_3H_5O + OH \qquad (25)$$

$$HO_2C_3H_5O \rightarrow C_3H_5O_2 + OH \qquad (26)$$

As can be seen from Reaction 23, this scheme provides a path for the formation of propene oxide, one of the major products observed in the experiments. However, the experimental results also showed that the propene oxide forms later than propene, while this reaction scheme has propene oxide forming earlier. Thus, the majority of the propene oxide is probably formed directly from propene. Therefore the alkylperoxy isomerization route is not very important in the propane oxidation mechanism. It will be shown later in this report that the alkylperoxy isomerization scheme is much more important for longer chain (higher carbon number) alkanes.

occur by reactions of the type such as 10, 11, and 12. Aldehydes are believed to be important in the hydroperoxide scheme in that they serve as hydrogen donors which contribute to rapid build-up of hydroperoxides. Acetaldehyde is the most important aldehyde in almost all combustion systems.

Another branching scheme that may contribute to the low temperature mechanism involves the acylperoxy radical (RCO_3) which is formed by O_2 addition to the acetyl radical. The acylperoxy radical can then abstract a hydrogen to form an acid:

$$RCO + O_2 \rightarrow RCO_3 \tag{16}$$

$$RCO_3 \xrightarrow{+H} RCO_3H \tag{17}$$

Branching takes place as the acid decomposes into two radicals:

$$RCO_3H \rightarrow RCO_2 + OH \tag{18}$$

According to Benson (1981), the RCO_3H is a very effective branching agent, decomposing even faster than ROOH. It should, therefore, rapidly accelerate the reaction. However, since the RCO_3H is dependent on the aldehyde concentration through RCO, its contribution to the branching will be felt mainly near the maximum rate where the aldehyde concentration is relatively high. Also, branching by this scheme is expected to be effective for lean conditions and only at low temperatures. As the temperature increases, direct decomposition of the acetyl radical will become favored

$$RCO + M \rightarrow R + CO + M \tag{19}$$

So that above about 620 K, branching by the acid route will be unimportant (Baldwin and Walker, 1973).

4. Alkylperoxy Isomerization

A key intermediate in the low temperature reaction is the alkylperoxy radical (RO_2). The many possible paths by which this species can react can of a cool flame and then diminish as the flame passes. Other studies (Walsh, 1946; Bardwell, 1955) have shown that hydroperoxides behave in the same manner.

More recently, cool flame studies by Salooja (1965) on isomeric hexanes and by Burgess and Laughlin (1967) on n-heptane have shown more conclusively that hydroperoxides are the main branching intermediate. This was confirmed most recently by Falconer et al. (1983) who have clearly demonstrated that hydroperoxides are the main branching agent for the cool flame oxidation of isobutane. In addition, they showed that aldehydes were not greatly involved in the degenerate branching mechanism. In the current study on propane, the experiment was not equipped to measure hydroperoxides, which are typically difficult to measure. However, the acetaldehyde concentration showed no significant decrease during the passage of the cool flames (Fig. 13). In other studies on propane oxidation, Bonner and Tipper (1965) and Falconer et al. (1983) detected hydroperoxides but in very small amounts.

Shtern has determined that a small amount of peroxide is able to yield the same branching rate as an amount of aldehyde 50 times as great (Shtern, 1964; and Pollard, 1977). Therefore, only very small amounts of peroxides are required to sufficiently accelerate the reaction. Since peroxides have been clearly shown to be the branching agents in the cool flame oxidation of alkanes with carbon number greater than 3, it is highly likely that propane would operate by the same mechanism. This is further confirmed by the experimental results which show that propane and higher carbon number alkanes display similar cool flame behavior.

Hydroperoxides are considered, therefore, to be the main branching intermediates. This is consistent with the view of Benson (1981), that hydroperoxides are the active intermediates and that propagation and branching

Thus, in this scheme, acetaldehyde is the stable branching intermediate.

Another possible branching route involves the decomposition of hydroperoxides. This theory was first postulated by Walsh (1947) and, as with the aldehyde route, involves the alkylperoxy radical. In this scheme, however, the alkylperoxy radical, instead of decomposing directly, first abstracts a hydrogen from the parent fuel or another hydrogen donor, such as an aldehyde, forming a hydroperoxide:

$$RO_2 + RH \rightarrow ROOH + R \tag{10}$$

$$RO_2 + RCHO \rightarrow ROOH + RCO \tag{11}$$

Chain branching then results as the hydroperoxide decomposes to the alkoxy and hydroxyl radicals:

$$ROOH \rightarrow RO + OH \tag{12}$$

Thus, for propane, the primary reactions are:

$$C_3H_7O_2 + C_3H_8 \rightarrow C_3H_7OOH + C_3H_7 \tag{13}$$

$$C_3H_7O_2 + CH_3CHO \rightarrow C_3H_7OOH + CH_3CO \tag{14}$$

$$C_3H_7OOH \rightarrow C_3H_7O + OH \tag{15}$$

Reaction 13 would be the major producer of the hydroperoxide in the early stages of the reaction due to the large concentration of propane. However, as acetaldehyde is produced, Reaction 14 becomes favored due to the relatively weaker C-H bond strength in the CHO group.

Many attempts have been made to test these two theories and confirm the identity of the branching intermediates as either aldehydes or hydroperoxides. Early experimental studies (Shtern, 1964; Batten and Ridge, 1955; and Bardwell, 1955) have demonstrated that the addition of each of these compounds to reacting systems decreased the induction period and accelerated the reaction. It has also been shown by Knox and Norrish (1954) and Norrish (1951) that aldehydes build up to a maximum concentration just prior to the passage about 473 K. This occurs because the position of equilibrium undergoes large changes with temperature. According to Baldwin and Walker (1973) the reversibility of Reaction 5 enables Reaction 6 to begin to compete above about 573 K. It will be shown that the competition between Reactions 5 and 6 contributes to the existence of the negative temperature coefficient phenomenon.

3. Branching Paths

As mentioned previously, the negative temperature coefficient represents a temperature regime over which a transition in the oxidation chemistry occurs, going from a low temperature mechanism to that of an intermediate temperature mechanism. The mechanism which operates at the lower temperatures (<650 K for alkanes in general), has been the subject of much controversy, particularly with regard to the identity of the branching intermediate responsible for the acceleration of the reaction and for the formation of cool flames. There are three possible routes which lead to chain branching in this temperature regime, two of which arise from reactions of the alkylperoxy radical.

It is believed that one of the many possible fates of the alkylperoxy radical is direct decomposition to an aldehyde and an alkoxy radical:

$$RO_2 \rightarrow RCHO + RO \qquad (7)$$

This step was postulated by Shtern (1964) and is also included in the Semenov mechanism (Glassman, 1977). According to Lewis and Von Elbe (1961), with propane as the fuel it is likely that only the $i\text{-}C_3H_7O_2$ radical will lead to these type products:

$$i\text{-}C_3H_7O_2 \rightarrow CH_3CHO + CH_3O \qquad (8)$$

Chain branching then occurs as the acetaldehyde reacts with O_2 producing the acetyl and hydroperoxyl radicals:

$$CH_3CHO + O_2 \rightarrow CH_3CO + HO_2 \qquad (9)$$

most pronounced at low temperatures (Fish, 1968). The distinction becomes less important as temperature increases. As the various radicals such as RO_2, HO_2, and OH are formed during the course of the reaction, they will take over and rapidly attack the initial fuel:

$$C_3H_8 + RO_2 \rightarrow C_3H_7 + ROOH \tag{2}$$

$$C_3H_8 + HO_2 \rightarrow C_3H_7 + H_2O_2 \tag{3}$$

$$C_3H_8 + OH \rightarrow C_3H_7 + H_2O \tag{4}$$

The OH radicals are the most reactive of these species; consequently attack by OH is much less selective than the attack by RO_2 and HO_2 which, in turn, is less selective than the attack by O_2. Therefore, Reaction 4 will tend to lead to a greater concentration of n-propyl radicals since the ratio of primary C-H bonds to secondary C-H bonds is 3:1. At low temperatures, however, the OH radicals are much less abundant than at high temperatures, so O_2, RO_2 and HO_2 attack will predominate. Thus, i-C_3H_7 will still be favored over n-C_3H_7 at low temperatures but n-C_3H_7 will be favored at high temperatures.

2. Propagation

The propagation process involves reactions of the propyl and other alkyl radicals. Direct unimolecular decomposition of these radicals may occur; however, these reactions will become important only at higher temperatures (>750 K). At low temperatures, the propyl radicals will react primarily with oxygen. This reaction can occur in two ways:

$$C_3H_7 + O_2 \rightarrow C_3H_7O_2 \tag{5}$$

$$C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2 \tag{6}$$

In Reaction 5, the oxygen adds to the propyl radical to form a propylperoxy radical. In Reaction 6, the oxygen abstracts a hydrogen to form the conjugate alkene, propene, and the hydroperoxyl radical. Although Reaction 5 is faster than Reaction 6 and is more favored at lower temperatures, Benson (1965, 1976, and 1981) has shown that reactions of this type are rapidly reversible above

C. CHARACTERISTICS OF THE LOW AND INTERMEDIATE TEMPERATURE OXIDATION MECHANISM

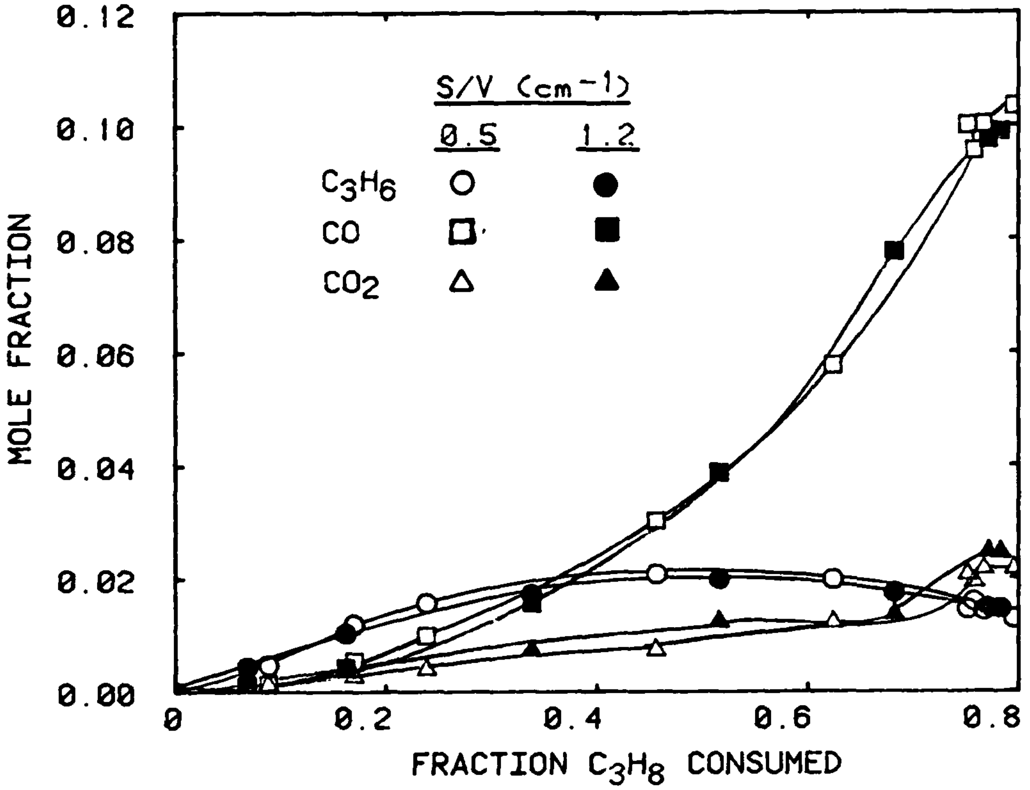
This section highlights the main reaction paths of the low and intermediate temperature propane mechanism. Reaction rate parameters for selected reactions listed in this section were either determined from the literature or estimated, and are given at the end of this section (Table III). These reactions are only a compilation of some existing and some new reactions which attempt to explain the existence and relative amounts of the various reaction products formed. They are not intended to comprise a complete mechanism. Consideration of the main reaction paths can be used to explain the negative temperature coefficient and the change in the observed products with temperature. For a description of detailed propane mechanisms, the reader is referred to the work of Westbrook and Pitz (1984), Jachimowski (1984), Warnatz (1983), and Cathonnet et al. (1981). However, these detailed models are primarily geared toward high temperature oxidation (T>1000 K). Thus, the reactions described in this section can be used along with other low temperature submechanisms (e.g., propionaldehyde and acetaldehyde (Kaiser et al., 1983, 1984)) to supplement and extend these high temperature kinetic models to lower temperatures.

1. Initiation and Radical Attack on the Fuel

The initial attack on the propane is that of hydrogen abstraction by O_2:

$$C_3H_8 + O_2 \rightarrow C_3H_7 + HO_2 \qquad (1)$$

This reaction is slow, selective and endothermic, having an activation energy of 47.6 kcal/mol (Walker, 1975) and, despite producing two radicals, does not greatly accelerate the reaction. The resulting propyl radicals should consist of both n-C_3H_7 and i-C_3H_7. The formation of i-C_3H_7, though, is favored as the secondary C-H bond strength is about 3 kcal less than that for a primary C-H bond. The effect of bond strength on the selectivity of attack is



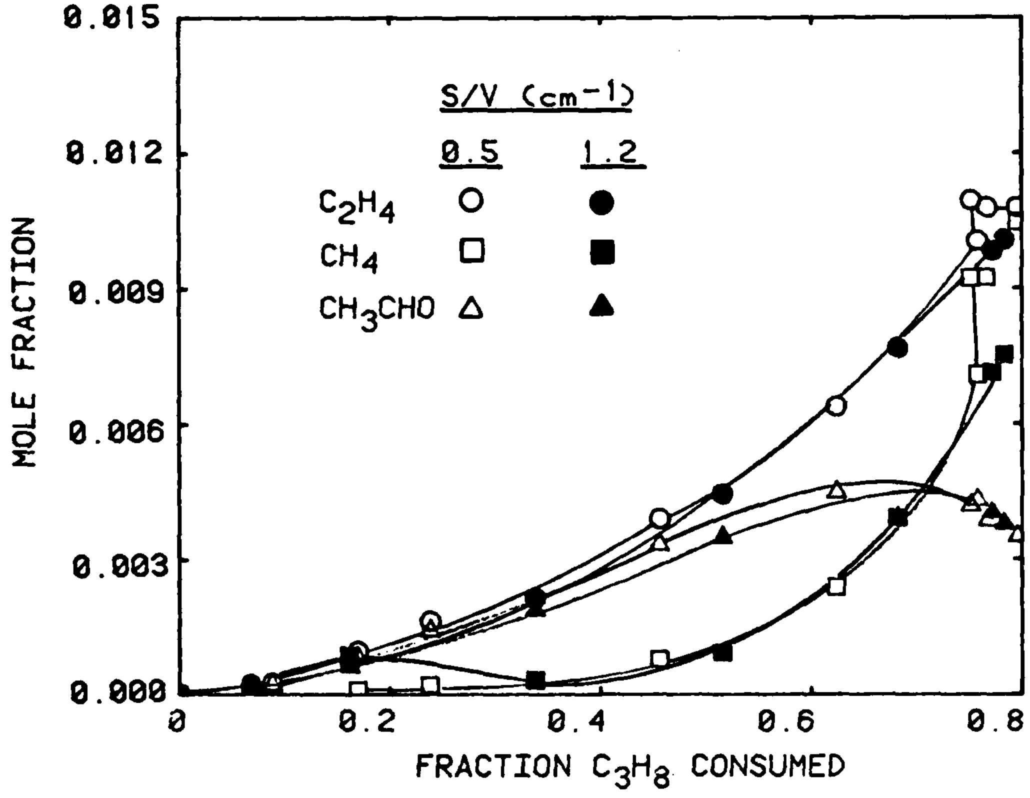


FIG. 22. EFFECT OF SURFACE-TO-VOLUME RATIO ON THE SPECIES CONCENTRATION PROFILES FOR C_3H_8/AIR MIXTURES AT $\phi=3.0$ P_o=600 TORR; T_o=683 K.

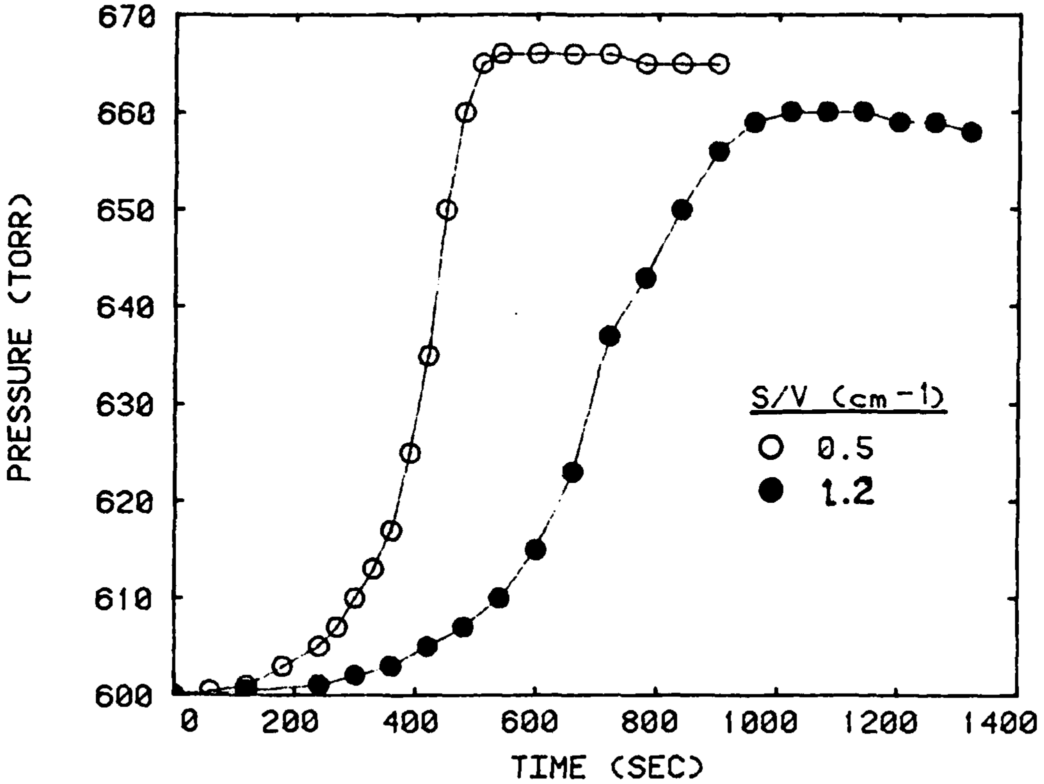


FIG. 20. EFFECT OF SURFACE-TO-VOLUME RATIO ON THE PRESSURE HISTORIES FOR C_3H_8/AIR MIXTURES AT ϕ=3.0; To=683 K.

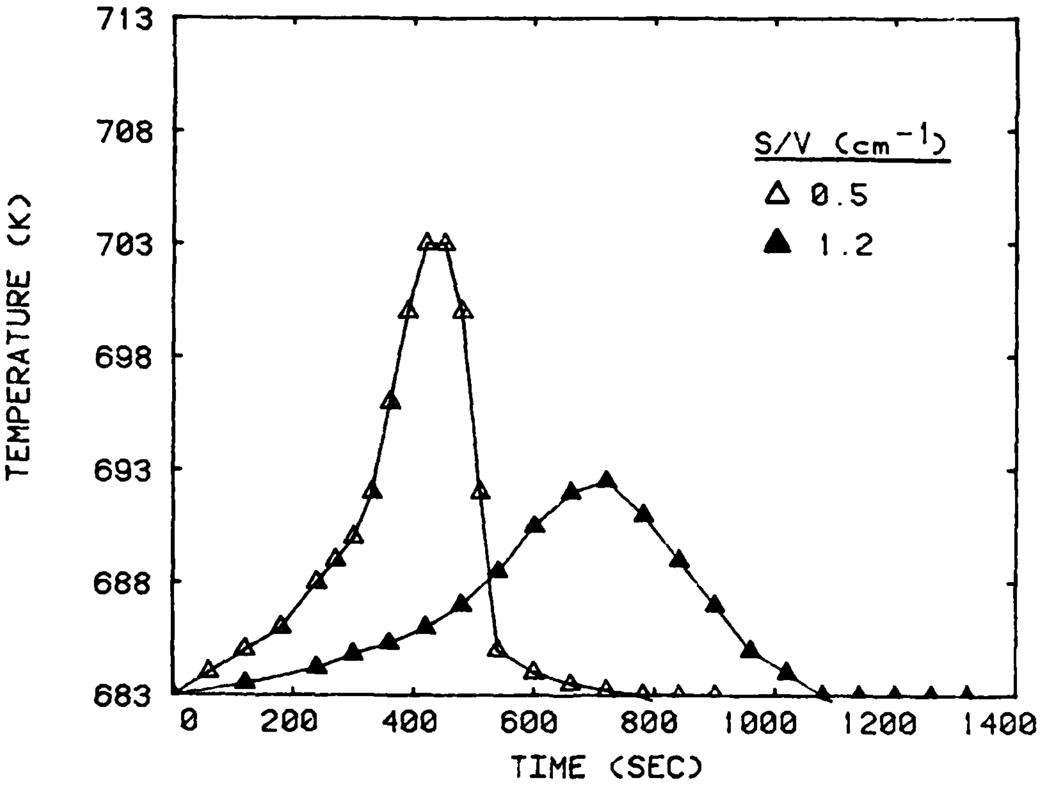
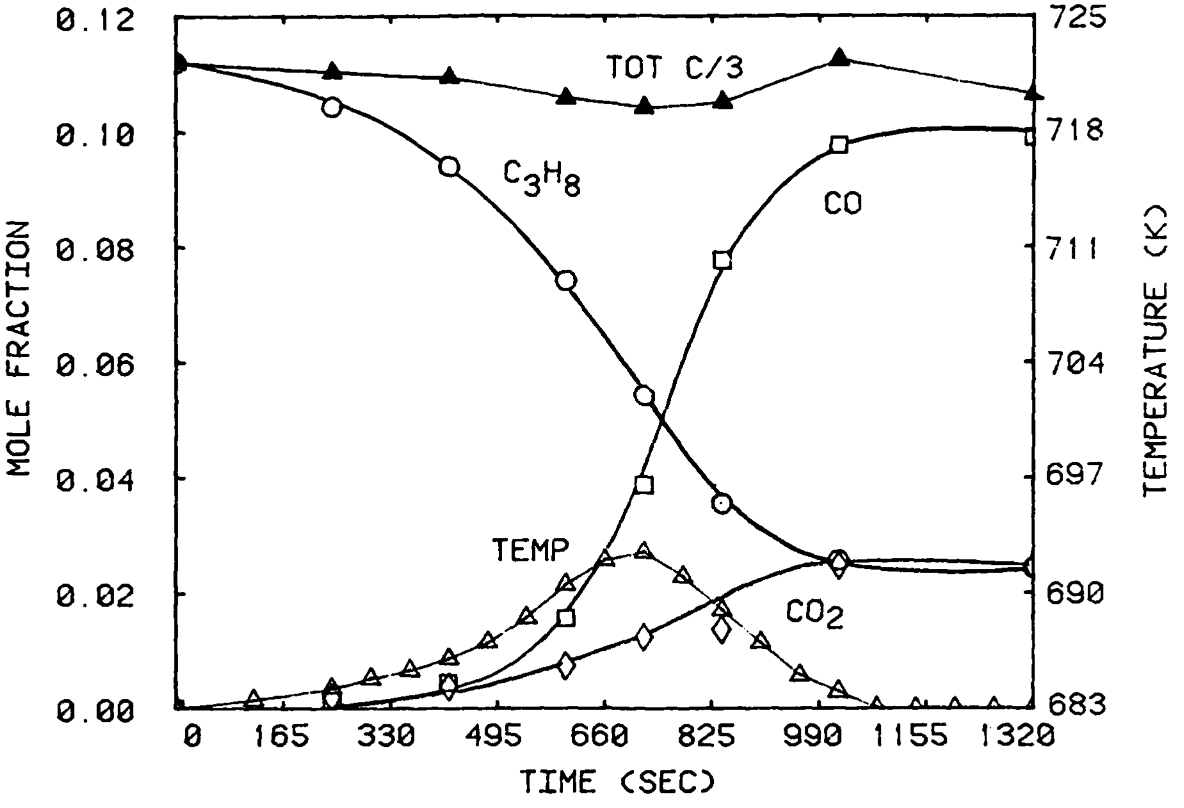


FIG. 21. EFFECT OF SURFACE-TO-VOLUME RATIO ON THE TEMPERATURE HISTORIES FOR C_3H_8/AIR MIXTURES AT ϕ=3.0; Po=600 TORR.



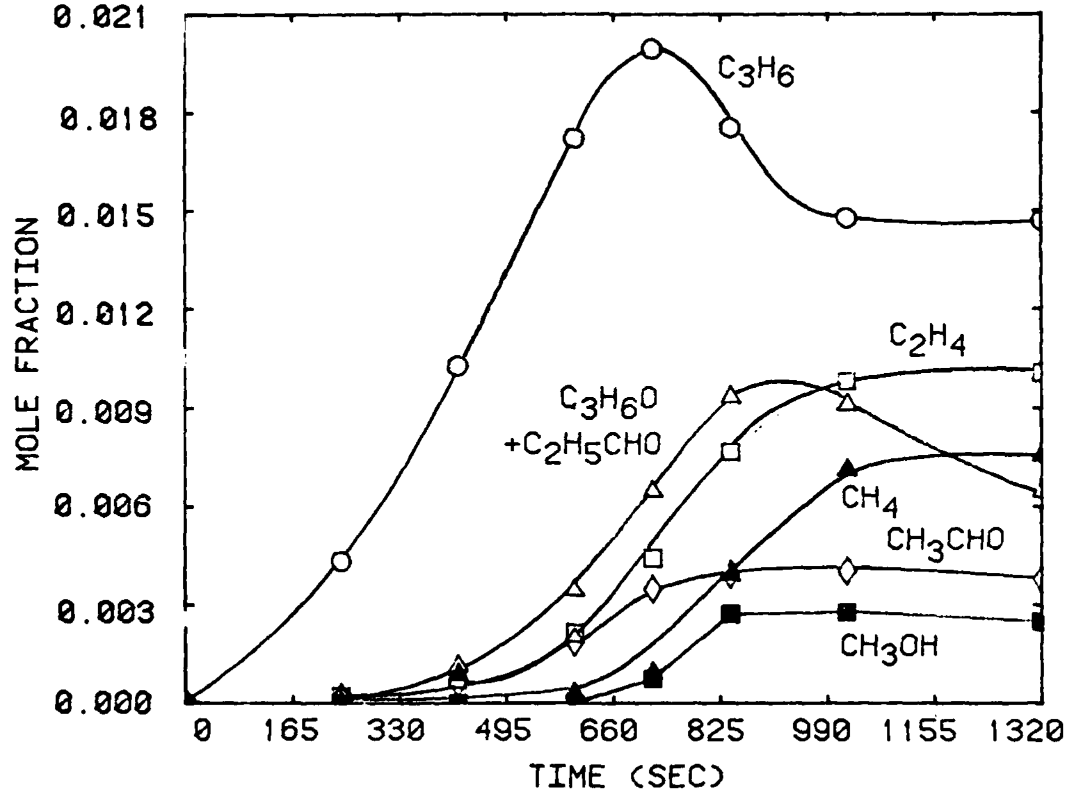
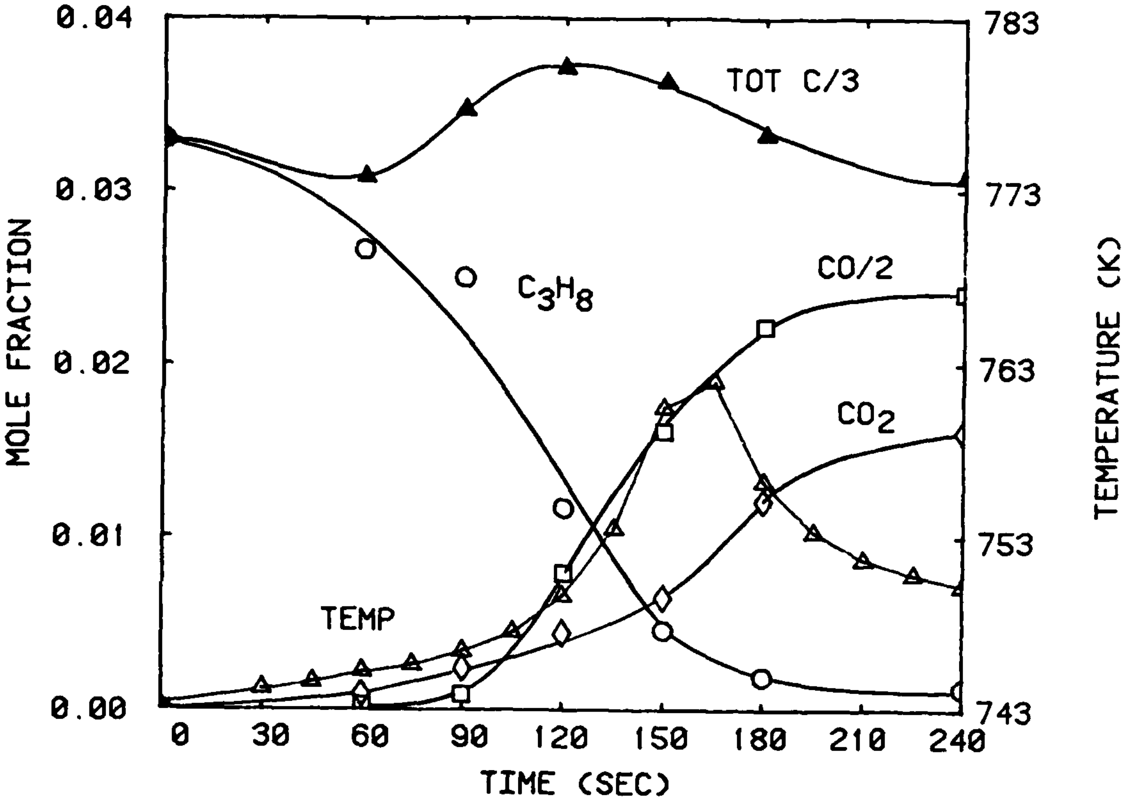


FIG. 19. SPECIES CONCENTRATION AND TEMPERATURE PROFILES FOR C_3H_8/AIR MIXTURES AT $\phi=3.0$; $P_o=600$ TORR; $T_o=683$ K. SURFACE-TO-VOLUME RATIO=1.2 cm^{-1}.

conditions as in Fig. 14. The species concentration and pressure and temperature profiles obtained for the higher S/V vessel are presented in Figs. 19, 20, and 21 respectively. From the species profiles it can be seen that the reaction in the higher S/V vessel is qualitatively very similar to the reaction in the lower S/V vessel. The same intermediates and products are formed at essentially the same stage of the reaction. Moreover, the quantities of products formed and fuel consumed are nearly the same in each case.

The two primary differences between the two cases involve the characteristic reaction times and the maximum temperatures. By comparison of the pressure and temperature profiles it can be seen that the overall reaction time and the induction period are longer for the higher S/V vessel. Also, the maximum temperature for the higher S/V case was only half that of the lower S/V case. This is believed not to be a direct thermal effect. Since the surface was increased by adding an insert and not by increasing the outside wall area, the effect of the extra surface as a heat sink was minimal. Instead, the added surface affected the reaction by serving as a sink for termination of radicals and branching agents, slowing the reaction and reducing the rate of heat release. However, in most combustion systems wall surface does act as a heat sink as well as sink for radicals and chain carriers.

In order to determine the extent of surface effects on the reaction path, species concentration profiles were plotted against the amount of fuel consumed (Fig. 22). These profiles are shown to be coincident for both S/V cases. Therefore it is concluded that the role of the surface is one of providing heterogeneous termination of branching chains, thus slowing the overall reaction. It does not affect the main reaction paths of the mechanism. This is consistent with the results of Affleck and Fish (1967) and Baldwin *et al.*, (1977).



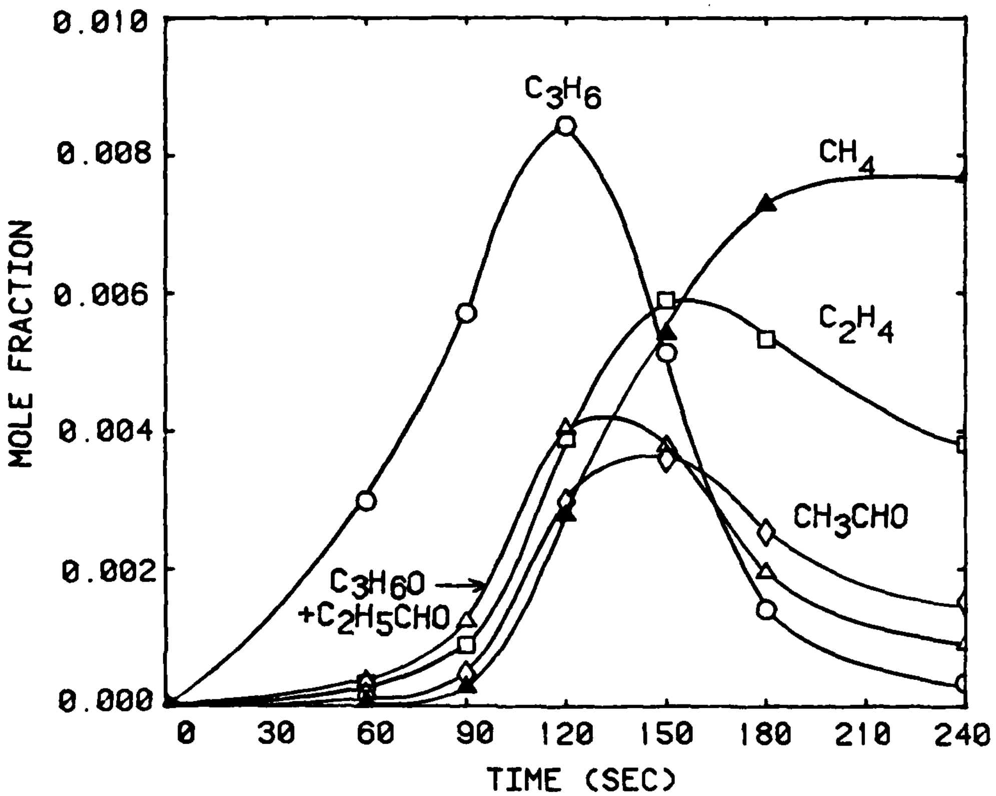


FIG. 18. SPECIES CONCENTRATION AND TEMPERATURE PROFILES FOR C_3H_8/AIR MIXTURES AT Φ =0.8; Po=600 TORR; To=743 K.

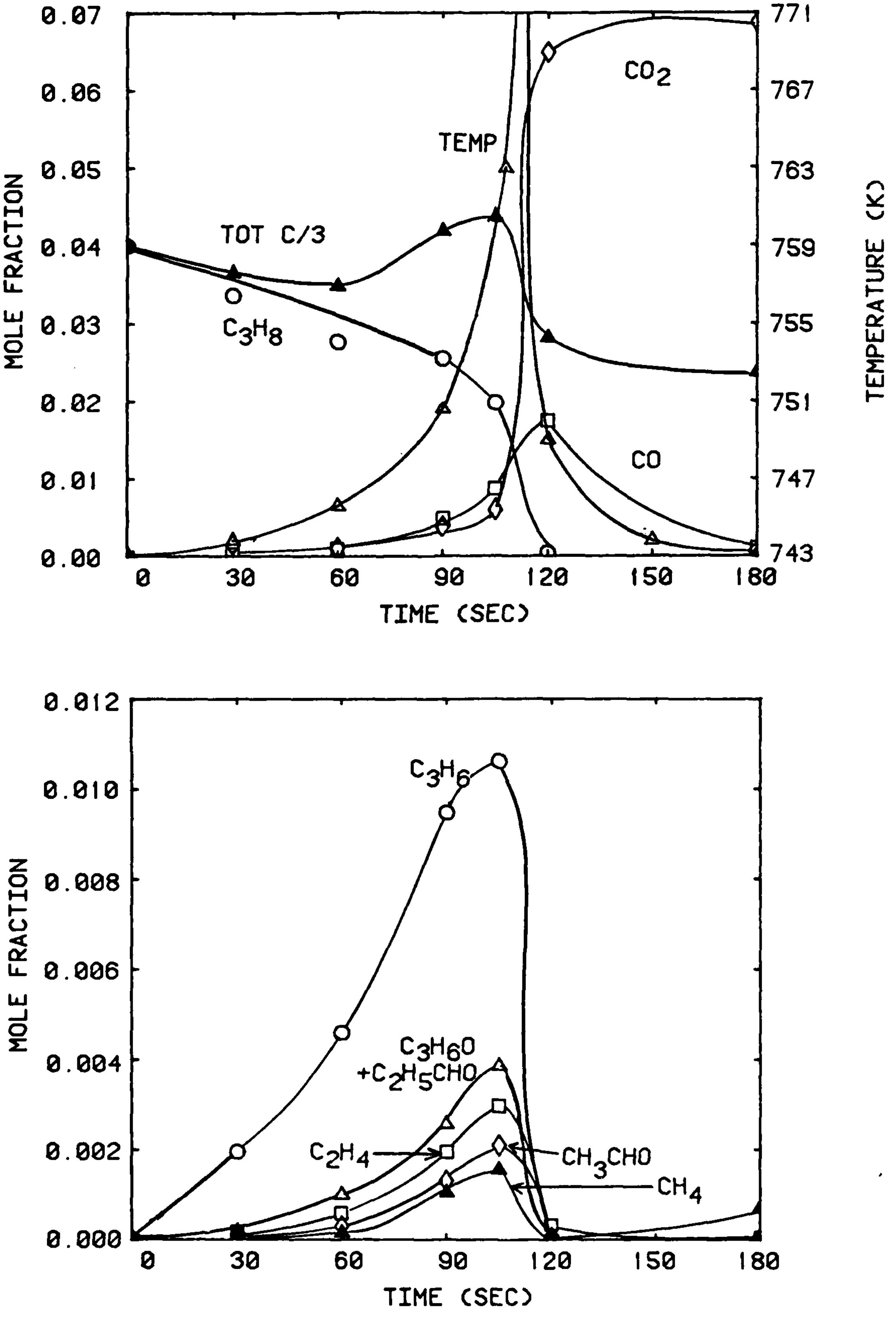


FIG. 17. SPECIES CONCENTRATION AND TEMPERATURE PROFILES FOR C_3H_8/AIR MIXTURES AT ϕ =1.0; Po=600 TORR; To=743 K.

unreactive NTC zone is again due the relative importance of Reactions 5 and 6. In the low temperature region, RO_2 radicals are abundant and lead to rapid acceleration of the reaction, as was seen, via ROOH which produces the very reactive OH radical. In the NTC region, Reaction 6 becomes important, producing the alkene and the HO_2 radical, which replaces RO_2 as the abundant radical. Even though HO_2 is more reactive than RO_2, it will not lead to rapid acceleration of the reaction in this temperature range, since it does not have as many reaction paths as does RO_2. HO_2 will tend mainly to abstract a hydrogen from a hydrogen donor such as the fuel or an aldehyde to form relatively stable hydrogen peroxide:

$$HO_2 \xrightarrow{+H} H_2O_2 \qquad (27)$$

From the experimental results, the NTC ends at 650 K for propane, beyond which the induction period decreases and the maximum rate increases with temperature (Figs. 7 and 8). The rate of hydrogen peroxide dissociation (Reaction 28) is very low below 650 K, but increases rapidly at higher temperatures.

$$H_2O_2 + M \rightarrow OH + OH + M \qquad (28)$$

Therefore this reaction is the main chain branching reaction at temperatures above the NTC region (>650 K). It is extremely accelerating, producing two very reactive hydroxyl radicals. Thus, the low temperature stability of H_2O_2 explains the existence of a region between 600 and 650 K as a separation and transition between two different accelerating mechanisms.

The reaction within the NTC region is still autocatalytic, exhibiting an induction period and an S-shaped pressure profile as do the reactions in both the low and intermediate temperature zones. Degenerate chain branching is still evident in the NTC range, but it probably proceeds at a diminishing rate due to the decreasing concentration of RO_2.

The shift in the tendency of the mechanisms to form oxygenated products at low temperatures (below the NTC zone) and alkanes and alkenes at the intermediate temperatures (above the NTC zone) can be explained by considering the main reaction paths in each of the regimes:

$$n\text{-}C_3H_7 + O_2 \rightarrow n\text{-}C_3H_7O_2 \qquad (5a)$$

$$i\text{-}C_3H_7 + O_2 \rightarrow i\text{-}C_3H_7O_2 \qquad (5b)$$

$$C_2H_5 + O_2 \rightarrow C_2H_5O_2 \qquad (29)$$

$$CH_3 + O_2 \rightarrow CH_3O_2 \qquad (30)$$

These addition reactions lead to the formation of oxygenated species. The propylperoxy radicals will be the most plentiful as they result from the parent fuel. $i\text{-}C_3H_7O_2$ will be favored over $n\text{-}C_3H_7O_2$ radicals due to the previously discussed bond energy considerations. The hydroperoxides formed from the propylperoxy radicals decompose to propoxy and hydroxyl radicals:

$$n\text{-}C_3H_7OOH \rightarrow n\text{-}C_3H_7O + OH \qquad (31)$$

$$i\text{-}C_3H_7OOH \rightarrow i\text{-}C_3H_7O + OH \qquad (32)$$

One possible reaction path of the propoxy radicals is reaction with oxygen, leading to C_3 oxirans, aldehydes, and ketones:

$$n\text{-}C_3H_7O + O_2 \rightarrow C_3H_6O + HO_2 \qquad (33)$$

$$n\text{-}C_3H_7O + O_2 \rightarrow CH_3CH_2CHO + HO_2 \qquad (34)$$

$$i\text{-}C_3H_7O + O_2 \rightarrow CH_3CH_2CHO + HO_2 \qquad (35)$$

$$i\text{-}C_3H_7O + O_2 \rightarrow CH_3COCH_3 + HO_2 \qquad (36)$$

The primary reaction path of the propoxy radicals, however, is probably direct decomposition. The different isomers though, will tend to yield different products:

$$n\text{-}C_3H_7O \rightarrow C_2H_5 + HCHO \qquad (37)$$

$$i\text{-}C_3H_7O \rightarrow CH_3CHO + CH_3 \qquad (38)$$

Acetaldehyde and methyl are the major products due to the relative dominance of the $i\text{-}C_3H_7O$ radicals.

The methylperoxy radical will also be important, forming from Reaction 30. This leads to methoxy production and ultimately to methanol formation through the following sequence of reactions:

$$CH_3O_2 \xrightarrow{+H} CH_3OOH \tag{39}$$

$$CH_3OOH \rightarrow CH_3O + OH \tag{40}$$

$$CH_3O \xrightarrow{+H} CH_3OH \tag{41}$$

Unlike the propoxy radicals, the methoxy radicals do not decompose readily and will primarily abstract a hydrogen to form methanol. The large amount of methanol observed experimentally at the low temperatures confirms the abundance of methoxy. Hydrogen abstraction by the propoxy radical is unlikely since no detectable amounts of the C_3 alcohols were observed.

The competing reactions to those forming the alkylperoxy radicals (Reactions 5a, 5b, 29, 30) are abstraction reactions:

$$n\text{-}C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2 \tag{6a}$$

$$i\text{-}C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2 \tag{6b}$$

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \tag{42}$$

$$CH_3 \xrightarrow{+H} CH_4 \tag{43}$$

At the low temperatures, these reactions are not as important as the oxygen addition reactions so mainly oxygenated products are formed. However, as the temperature increases, Reactions 6a, 6b, 42 and 43 become faster, leading to increased production of HO_2, the conjugate alkenes and methane and to decreased production of RO_2 and the oxygenated hydrocarbon products.

One exception to this is with the propene oxide. The yield of propene oxide actually increases with temperature. This can be explained by the fact that at the intermediate temperatures, propene is the major hydrocarbon species produced. This can lead to increased propene oxide production by way of the reaction:

$$C_3H_6 + HO_2 \rightarrow C_3H_6O + OH \qquad (44)$$

This reaction illustrates the importance of secondary reactions involving the major intermediates such as propene. It is believed that the subsequent oxidation of propene is very important in the propane mechanism. This is true especially in the intermediate temperature region where large amounts of propene are formed from Reactions 6a and 6b. In view of this, studies were made on the low temperature oxidation of propene. These studies are described in Section IV.

6. Termination

The termination of the chain reactions at the low and intermediate temperatures can occur in two ways: homogeneously and heterogeneously. Homogeneous termination can occur as a result of radical recombination. At low temperatures, this would involve the reaction of RO_2:

$$RO_2 + RO_2 \rightarrow ROOH + Q + O_2 \qquad (45)$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \qquad (46)$$

At higher temperatures it would involve reactions of HO_2:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (47)$$

Radical recombination reactions can also result in the formation of higher alkanes:

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (48)$$

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10} \qquad (49)$$

Both ethane and butane were observed, in small amounts, in the products of propane oxidation.

Heterogeneous termination results from the diffusion of radicals ($\dot{R}O_2$, HO_2, OH) or branching agents (ROOH, H_2O_2) to the vessel surface where they are adsorbed or converted to inactive products (Fish, 1968). Diffusion controlled heterogeneous termination becomes less important as the pressure is increased. This is due to the inverse dependence of the molecular diffusivity on pressure. Thus at higher pressures, the rate of diffusion of radicals such as HO_2 to the walls is reduced, allowing them more time to react in the gas phase. The amount of surface can have a significant effect on heterogeneous termination. This effect was seen earlier in the report where the added surface area slowed the reaction although it did not qualitatively or quantitatively alter the reaction products.

7. Carbon Monoxide and Carbon Dioxide

There was relatively little change in the yields of both CO and CO_2 as the temperature increased from 583 to 683 K. However, examination of the mechanism shows that the reaction paths of these species undergo significant changes with temperature. At the low temperatures, these species are formed by the following sequence of reactions:

$$HCO + O_2 \rightarrow CO + HO_2 \tag{50}$$

$$CH_3CO + O_2 \rightarrow CH_3CO_3 \tag{51}$$

$$CH_3CO_3 \xrightarrow{+H} CH_3CO_3H \tag{52}$$

$$CH_3CO_3H \rightarrow CH_3CO_2 + OH \tag{53}$$

$$CH_3CO_2 \rightarrow CH_3 + CO_2 \tag{54}$$

$$CH_3CO_3 \rightarrow CH_3O + CO_2 \tag{55}$$

CO_2 results indirectly from O_2 addition to the acetyl radical. As the temperature increases though, direct decomposition of the acetyl radical becomes favored over the oxygen addition route:

$$CH_3CO + M \rightarrow CH_3 + CO + M \tag{56}$$

This reaction replaces the CO_2 formation route and instead leads to the production of more CO. From this it would be expected that, as the temperature increases, the yield of CO would increase, while that of CO_2 would decrease.

However, this is contrary to the experimental results which showed that the amounts formed of each of these species was essentially constant with temperature from 583 to 683 K. In addition, in the intermediate temperature regime, the net yields of CO decreased while that of the CO_2 increased with increasing temperature.

It is apparent then that upon entering the intermediate temperature regime, additional reactions which consume CO and produce CO_2 are becoming significant. Two important ones are:

$$CO + HO_2 \rightarrow CO_2 + OH \tag{57}$$

$$CO + OH \rightarrow CO_2 + H \tag{58}$$

These reactions provide routes for the conversion of CO to CO_2 and serve to better explain the experimental results. Of these two reactions, Reaction 57 will be most prominent at temperatures in the range 650-1000 K, where HO_2 radicals are abundant. At high temperatures, above about 1000 K, OH is the dominant radical with contributions from O and H radicals. At these temperatures, conversion of CO to CO_2 will occur almost exclusively by Reaction 58. Thus, at intermediate and high temperatures, CO_2 results from CO oxidation, whereas at low temperatures CO_2 does not go through CO but is formed directly from reactions of the acetyl and acylperoxy radicals.

A major portion of the heat release in a combustion reaction occurs as a result of the oxidation of CO to CO_2, following the sequential breakdown of the initial fuel into the intermediates H_2 and CO. At low temperatures, such as the range examined in this study, this conversion of CO to CO_2 does not occur to any great extent as seen by the high concentrations of CO and the relatively low concentrations of CO_2 at the end of the reaction. Therefore, the heat release is low, producing temperatures rises of only 30 to 40 degrees.

8. Comparison to the High Temperature Mechanism

It is interesting to note the changes in the mechanism with temperature. It has been shown in this report that the mechanism undergoes a significant change at about 650 K, going from a low temperature regime dominated by RO_2 radicals and addition reactions, to an intermediate temperature regime dominated by HO_2 radicals and abstraction reactions. Another major change occurs at about 900 to 1200 K, depending on the pressure. Here the mechanism goes from an intermediate temperature mechanism controlled by HO_2 to a high temperature mechanism controlled by OH. Unimolecular decomposition of radicals also becomes more important and the reaction becomes very fast. Some of the important characteristics of each of these temperature regimes are summarized in Table II. For all regimes, the fuel consumption route is abstraction of H by the dominant radical.

TABLE II. Characteristics of the Propane Oxidation Mechanism in Different Temperature Regimes at Low Pressures

	Temperature Regime		
	Low (<600 K)	Intermediate (650-1000 K)	High* (>1000 K)
Dominant Radical	RO_2	HO_2	OH, O, H
Characteristic Radical Reactions	Addition	Abstraction	Decomposition
Branching Agent	ROOH	H_2O_2	R
Branching Route	$ROOH \rightarrow RO + OH$	$H_2O_2+M \rightarrow 2OH+M$	$H+O_2 \rightarrow OH+O$

* The temperature separating the intermediate and high temperature reaction regimes is not well defined and still needs to be determined; it may extend as low as 800-900K, depending on the pressure.

It should be stressed that the information contained in Table II represents a qualitative generalization highlighting some of the changes in the propane mechanism with temperature at low pressures. It is expected that the transition temperatures for each reaction regime are likely to shift to higher temperatures as the pressure is increased.

In the low and intermediate temperature regimes (550-650 K and 650-1000 K), increasing the equivalence ratio accelerated the reaction, as seen in Figs. 7 and 8. This behavior is consistent with the mechanism when the main paths that accelerate the reaction are considered. At low temperatures, where RO_2 is dominant, the main accelerating route occurs by:

$$RH + RO_2 \rightarrow R + ROOH \tag{10}$$

$$ROOH \rightarrow RO + OH \tag{12}$$

As the fuel concentration is increased, more hydroperoxides are produced, providing chain branching and accelerating the reaction. This is confirmed by the cool flame behavior. Both the number and intensity of the cool flames increased with equivalence ratio.

In the intermediate temperature regime, where HO_2 is dominant, the main accelerating path occurs by:

$$C_3H_8 + HO_2 \rightarrow C_3H_7 + H_2O_2 \tag{59}$$

$$H_2O_2 + M \rightarrow OH + OH + M \tag{28}$$

As the equivalence ratio is increased, more hydrogen peroxide is formed in Reaction 59 which leads to chain branching by Reaction 28, thereby accelerating the reaction (Pitz and Westbrook, 1983).

In the high temperature regime ($T>1000$ K), the reaction displays a different behavior. The oxidation process is slowed as the equivalence ratio is increased. Pitz and Westbrook (1983) have attributed this behavior to the competition between two reactions:

$$C_3H_8 + H \rightarrow C_3H_7 + H_2 \tag{60}$$

$$H + O_2 \rightarrow OH + O \tag{61}$$

When the equivalence ratio is increased, the additional fuel gives rise to competition for H atoms between Reactions 60 and 61. Thus the overall reaction is slowed.

Another feature which distinguishes the different temperature regimes is the major hydrocarbon intermediate formed. In the low temperature regime it was shown that oxygenated hydrocarbons, methanol in particular, are the main intermediates. In the intermediate temperature regime propene was the main hydrocarbon intermediate. In studies made on propene oxidation at high temperatures by Hautman et al. (1981), ethene was found to be the principal hydrocarbon intermediate.

These different observations in the intermediate and high temperature regimes can be easily explained by considering the major reactions of the propyl radicals and how they are affected by temperature. At intermediate temperatures, the propyl radicals react with oxygen to form propene:

$$n\text{-}C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2 \tag{6a}$$

$$i\text{-}C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2 \tag{6b}$$

while at higher temperatures the propyl radicals primarily decompose unimolecularly:

$$n\text{-}C_3H_7 \rightarrow C_2H_4 + CH_3 \tag{62}$$

$$i\text{-}C_3H_7 \rightarrow C_3H_6 + H \tag{63}$$

with the n-propyl radical becoming favored as temperature increases, thus favoring the formation of ethene.

TABLE III. Selected Reactions and Rate Parameters for Low and Intermediate Temperature Propane Oxidation

Reaction Rates in lit, mol, sec, kcal units

$k=AT^n\exp(-Ea/RT)$

Reaction	$\log_{10} A$	n	Ea	Reference
$C_3H_8+O_2 \rightarrow nC_3H_7+HO_2$	11.1	0	50.6	Estimated*
$C_3H_8+O_2 \rightarrow iC_3H_7+HO_2$	10.6	0	47.6	Walker (1975)
$C_3H_8+OH \rightarrow nC_3H_7+H_2O$	5.68	1.4	0.85	Westbrook and Pitz (1984) and Tully *et al.* (1983)
$C_3H_8+OH \rightarrow iC_3H_7+H_2O$	5.76	1.4	0.85	Westbrook and Pitz (1984) and Tully *et al.* (1983)
$C_3H_8+HO_2 \rightarrow nC_3H_7+H_2O_2$	8.47	0	14.9	Cathonnet *et al.* (1981) and Walker (1977)
$C_3H_8+HO_2 \rightarrow iC_3H_7+H_2O_2$	7.99	0	12.6	Cathonnet *et al.* (1981) and Walker (1977)
$nC_3H_7+O_2 \rightarrow nC_3H_7O_2$	9.0	0	0	Benson (1981)
$iC_3H_7+O_2 \rightarrow iC_3H_7O_2$	9.0	0	0	Benson (1981)
$nC_3H_7O_2 \rightarrow nC_3H_7+O_2$	14.5	0	28.0	Dechaux (1981) and Benson (1976)
$iC_3H_7O_2 \rightarrow iC_3H_7+O_2$	14.5	0	28.0	Dechaux (1981) and Benson (1976)
$nC_3H_7+O_2 \rightarrow C_3H_6+HO_2$	8.5	0	6.0	Benson (1981)
$iC_3H_7+O_2 \rightarrow C_3H_6+HO_2$	8.5	0	6.0	Benson (1981)
$iC_3H_7O_2 \rightarrow CH_3CHO+CH_3O$	13.0	0	25.0	Dechaux (1981)
$nC_3H_7O_2+C_3H_8 \rightarrow nC_3H_7OOH+nC_3H_7$	9.0	0	19.4	Walker (1978)
$iC_3H_7O_2+C_3H_8 \rightarrow iC_3H_7OOH+iC_3H_7$	9.0	0	17.1	Walker (1978)
$nC_3H_7O_2+C_3H_8 \rightarrow nC_3H_7OOH+iC_3H_7$	9.0	0	17.1	Walker (1978)

TABLE III. (cont'd)

Reaction	log A	n	Ea	Reference
$iC_3H_7O_2+C_3H_8 \rightarrow iC_3H_7OOH+nC_3H_7$	9.0	0	19.4	Walker (1978)
$nC_3H_7O_2+CH_3CHO \rightarrow nC_3H_7OOH+CH_3CO$	9.0	0	9.0	Dechaux (1981)
$iC_3H_7O_2+CH_3CHO \rightarrow iC_3H_7OOH+CH_3CO$	9.0	0	9.0	Dechaux (1981)
$nC_3H_7OOH \rightarrow nC_3H_7O+OH$	15.6	0	43.0	Benson (1981)
$iC_3H_7OOH \rightarrow iC_3H_7O+OH$	15.6	0	43.0	Benson (1981)
$nC_3H_7O+O_2 \rightarrow C_3H_6O+HO_2$	8.5	0	4.0	Dechaux (1981)
$nC_3H_7O+O_2 \rightarrow C_2H_5CHO+HO_2$	8.5	0	4.0	Dechaux (1981)
$iC_3H_7O+O_2 \rightarrow C_2H_5CHO+HO_2$	8.5	0	4.0	Dechaux (1981)
$iC_3H_7O+O_2 \rightarrow CH_3COCH_3+HO_2$	8.5	0	4.0	Dechaux (1981)
$iC_3H_7O \rightarrow CH_3CHO+CH_3$	14.6	0	17.2	Bogan *et al.* (1983) and Batt (1979)
$nC_3H_7O \rightarrow C_2H_5+HCHO$	14.6	0	17.2	Est. from above reaction
$nC_3H_7O_2 \rightarrow C_3H_6OOH$	12.1	0	38.0	Walker (1975)
$C_3H_6+HO_2 \rightarrow C_3H_6O+OH$	9.0	0	14.2	Baldwin *et al.*(1985)
$CH_3CHO+O_2 \rightarrow CH_3CO+HO_2$	10.3	0	39.0	Walker (1975)

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* Estimated by analogy with the reaction $C_3H_8 + O_2 \rightarrow iC_3H_7 + HO_2$ (Walker, 1975). 3 kcal were added to the activation energy to account for the higher bond strength of primary C-H bonds. log 3 was added to the pre-exponential to account for 3:1 ratio of primary to secondary C-H bonds.

IV. PREIGNITION OXIDATION CHARACTERISTICS OF PROPENE

A. INTRODUCTION

From the work on propane described in Section III of this report, it was determined that many of the intermediates formed are, themselves, highly reactive fuels as well. As they are formed from the breakdown of the parent fuel, they also react and become the sources of secondary products. Thus, even for a relatively simple fuel such as propane, the oxidation process involves the complex interaction of a large number of chemical species entering into concurrent and competing reactions.

One of the most important intermediates in the low and intermediate temperature oxidation of propane is propene. Propene is also an important intermediate in the oxidation of higher molecular weight alkanes such as n-butane and iso-butane. Propene and other alkenes are, in general, highly reactive and, since they are formed in the early stages of the reaction, they compete with the parent fuel for radicals and oxygen and become major sources of secondary products.

The oxidation of propene at low and intermediate temperatures has received only a moderate amount of attention. Early experimental studies by Bawn and Skirrow (1955) and Mullen and Skirrow (1958) identified the major reaction products and showed that the overall oxidation reaction was a degenerate branching type. Satterfield and Reid (1955) determined the presence of propene in oxidizing propane mixtures had an accelerating effect in the initial stages of the reaction but an inhibiting effect in the later stages. This behavior was attributed to the structure of the propene, which has a relatively weak C-H bond in the α position to the double bond. Thus, hydrogen abstraction occurs fairly easily, but once the initial hydrogen has been removed, a relatively stable allyl radical results, inhibiting the reaction. In another study, Nguyen _et al._ (1970) examined mixtures of propane and propene. It was found that the addition of propene to propane resulted in an increase in the maximum reaction rate up to a point, and then further addition caused the maximum rate to decrease. More recently, Baldwin and Walker (1981, 1985) elucidated some of the elementary steps in the oxidation of several alkenes including propene. This work drew attention to the importance of radical addition reactions in alkene oxidation and produced some much needed rate constants.

In view of the importance of propene oxidation and the need for additional experimental studies, another phase of this research program was devoted to the study of the preignition oxidation characteristics of propene.

B. EXPERIMENTAL RESULTS AND DISCUSSION

1. Cool Flames and Negative Temperature Coefficient

The experimental results indicate that the oxidation of propene, as expected, has the characteristics of an autocatalytic reaction. This behavior can be seen by examination of the measured pressure histories (Figs. 23 and 24) obtained during the course of the reaction of propene and air at various initial conditions. The curves have the characteristic S-shape, displaying a well-defined induction period followed by a rapid pressure rise. The induction period also corresponded to the time for any significant fuel consumption to occur and it was found that the time of maximum rate measured by pressure rise was the same as that measured by fuel consumption. Thus, there was a direct correlation between the pressure rise and the propene consumption, and the rate of change of pressure is proportional to the overall reaction rate. The effect of experimental conditions on the overall reaction can be seen in Figs. 23 and 24. Increasing either the initial temperature or equivalence ratio has the effect of decreasing the induction period, increasing the maximum overall rate, and increasing the final pressure.

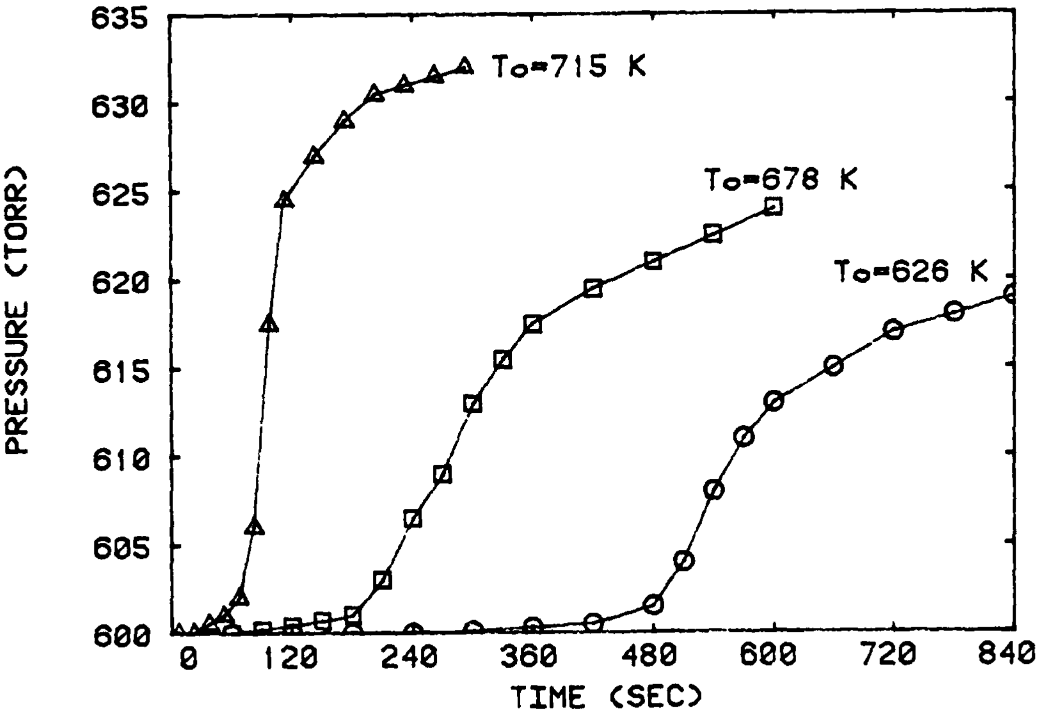


FIG. 23. EFFECT OF INITIAL TEMPERATURE ON THE PRESSURE HISTORIES FOR C_3H_6/AIR MIXTURES AT ϕ =0.8.

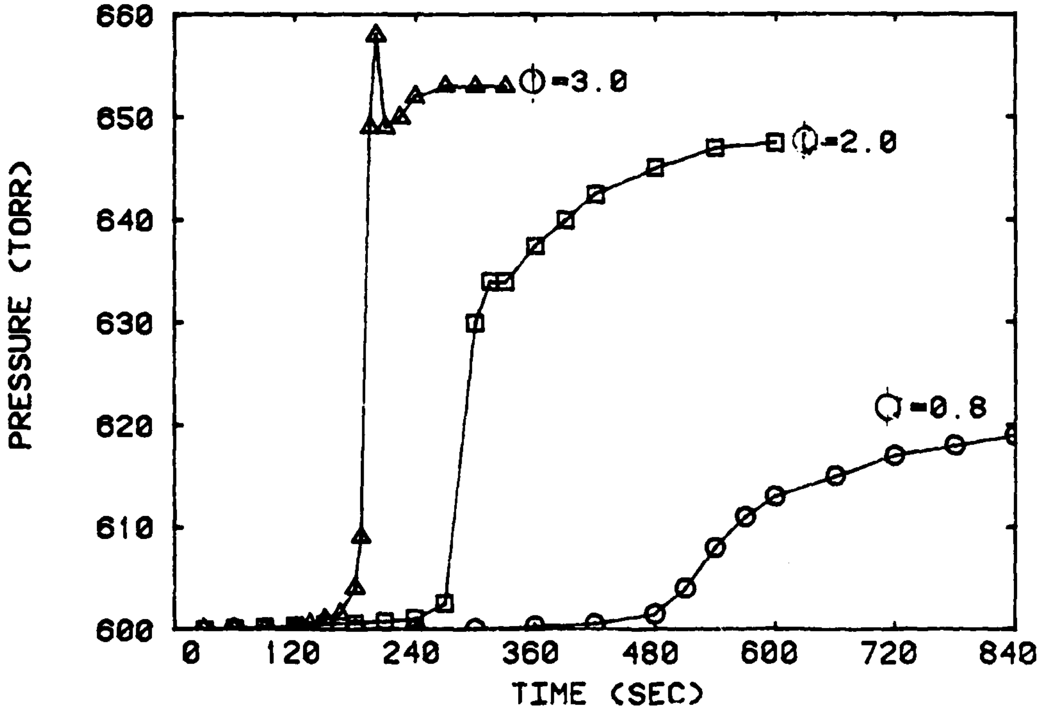


FIG. 24. EFFECT OF EQUIVALENCE RATIO ON THE PRESSURE HISTORIES AND COOL FLAMES FOR C_3H_6/AIR MIXTURES AT To=626 K.

$$C_3H_5 \rightarrow C_3H_4 + H \quad (94)$$

$$C_3H_5 + O_2 \rightarrow C_3H_4 + HO_2 \quad (81)$$

$$C_3H_5 + H \rightarrow C_3H_4 + H_2 \quad (95)$$

$$C_3H_5 + CH_3 \rightarrow C_3H_4 + CH_4 \quad (96)$$

Each of these reactions leads to the production of allene or propyne. Burcat and Radhakrishnan (1985) have determined that Reaction 81 is not important at high temperatures. Also, Westbrook and Pitz (1984) have determined that Reactions 95 and 96 should be favored over Reaction 94 due to the stability of the allyl radical.

These reaction paths explain the presence of C_2H_2 and C_3H_4 observed in the high temperature experiment. Abstraction reactions are less favored at the lower temperatures, due mainly to their high activation energies, allowing addition reactions to dominate as found in the present experimental study.

4. Comparison to Propane Oxidation

In this section, the results from the preignition studies on propene will be compared with those from propane in order to elucidate the important differences in the oxidation process of each fuel and to determine the effect of the presence of propene on propane oxidation.

Fig. 31 shows the effet of initial temperature on the induction period for both propane/air and propene/air mixtures each at an equivalence ratio of 2.0. Although both fuels display a negative temperature coefficient, propane has a wider NTC region and the effect of the NTC is more pronounced as seen from the magnitude of the decrease in induction period.

Comparison of the induction periods for each fuel produced different results in each of the temperature regimes. In the low temperature regime, the propene is less reactive (longer induction periods) than the propane. But in the intermediate temperature regime, the propene is more reactive

As with alkanes, chain branching at the intermediate temperatures proceeds by the decomposition of hydrogen peroxide:

$$H_2O_2 + M \rightarrow OH + OH + M \qquad (28)$$

Thus, the NTC region is still due to H_2O_2 but occurs over a smaller temperature range, probably because Reactions 82-86 are slower than Reactions 6a and 6b.

3. Comparison to the High Temperature Mechanism

There are significant differences in the propene oxidation mechanism between the low and high temperature reaction regimes. These differences are due mainly to the dominance of thermal decomposition reactions of the fuel and radicals at the high temperatures, as opposed to the lower temperatures where radical addition reactions are favored.

In a recent shock tube study of propene oxidation at temperatures from about 1300 to 1700 K (Burcat and Radhakrishnan, 1985), the major reaction products before ignition included ethene, methane, allene, propyne, and acetylene (the most abundant species). These products can be explained by considering the reactions of propene and allyl.

At high temperatures, the propene will tend to decompose unimolecularly by two possible reactions:

$$C_3H_6 \rightarrow C_3H_5 + H \qquad (91)$$

$$C_3H_6 \rightarrow C_2H_3 + CH_3 \qquad (92)$$

Reaction 92 is favored (Westbrook and Pitz, 1984) and leads to reactive vinyl radicals. Acetylene is then formed by hydrogen abstraction from vinyl:

$$C_2H_3 \xrightarrow{-H} C_2H_2 \qquad (93)$$

There are several reaction paths for allyl radical consumption at high temperatures. These consist of unimolecular decomposition and bimolecular abstraction:

$$C_3H_7 + O_2 \rightarrow C_3H_7O_2 \tag{5}$$

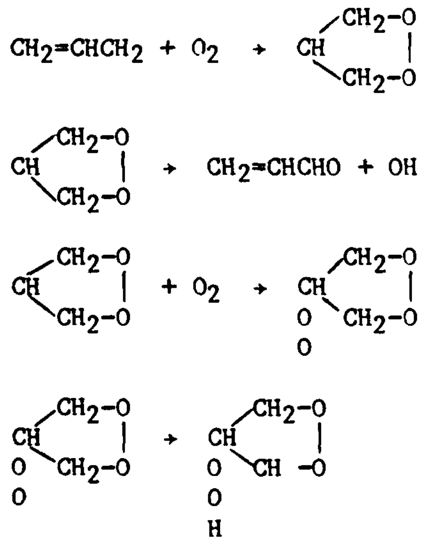
$$C_3H_7 + O_2 \rightarrow C_3H_6 + HO_2 \tag{6}$$

The analogous reactions for propene are:

$$C_3H_5 + O_2 \rightarrow C_3H_5O_2 \tag{80}$$

$$C_3H_5 + O_2 \rightarrow C_3H_4 + HO_2 \tag{81}$$

In actuality, Reaction 81 for propene must be ruled out at these temperatures since the experimental results indicated no formation of C_3H_4 (propyne or allene). This finding was confirmed by the results of Baldwin and Walker (1981). Thus, an alternative to Reaction 81 is needed to compete with Reaction 80. Baldwin and Walker (1981) postulated the following alternative sequence of reactions of allyl and O_2:



(82)

(83)

(84)

(85)

$$\rightarrow 2HCO + HCHO + OH \tag{86}$$

The products formed from Reaction 86 will oxidize rapidly and lead to increased production of CO, HO_2, and H_2O_2:

$$HCHO + O_2 \rightarrow CHO + HO_2 \tag{87}$$

$$CHO + O_2 \rightarrow CO + HO_2 \tag{88}$$

$$HCHO + HO_2 \rightarrow CHO + H_2O_2 \tag{89}$$

$$CHO + HO_2 \rightarrow CO + H_2O_2 \tag{90}$$

Concurrent with the propagation and branching processes which result from the allyl radical, other routes involving lower radicals also occur. One such path, which is certain to be present at low temperatures, results from the methyl radical:

$$CH_3 + O_2 \rightarrow CH_3O_2 \tag{30}$$

$$CH_3O_2 + C_3H_6 \rightarrow CH_3OOH + C_3H_5 \tag{79}$$

$$CH_3OOH \rightarrow CH_3O + OH \tag{40}$$

This path was shown to be important in propane oxidation in the low temperature regime. It is also important in propene oxidation and is responsible for the production of methanol:

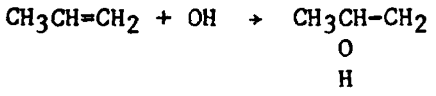
$$CH_3O \xrightarrow{+H} CH_3OH \tag{41}$$

Determination of the propagation and branching paths for propene oxidation in the intermediate temperature regime is difficult. It was shown that propene does exhibit a region of negative temperature coefficient from about 630-650 K. Thus, a transition in the mechanism is expected to occur as the temperature is increased across the region. This was certainly indicated by the effect of temperature on the reaction products formed. In particular, the net yields of the oxygenated products such as acetaldehyde and formaldehyde decreased across the NTC region while that of the lower alkanes and alkenes such as methane and ethene increased.

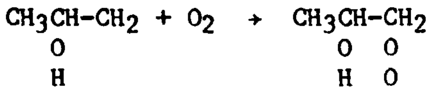
If one attempts to use the analogy with alkane oxidation to explain the mechanism transition, it does not work. As was seen in Section III for alkanes such as propane, the NTC and mechanism transition is due to the competition between O_2 addition to the alkyl radical and hydrogen abstraction by O_2. The former process is favored at low temperatures, while the latter is favored at intermediate temperatures:

of acetaldehyde and methyl should be favored slightly.

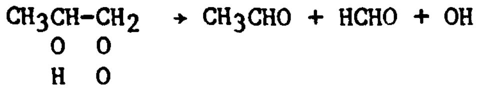
Ray and Waddington (1973) have determined that aldehydes may also be formed by OH addition to alkenes followed by O_2 addition. Thus for propene:



$$CH_3CH{=}CH_2 + OH \rightarrow CH_3\underset{\underset{H}{O}}{CH}{-}CH_2 \qquad (72)$$



$$CH_3\underset{\underset{H}{O}}{CH}{-}CH_2 + O_2 \rightarrow CH_3\underset{\underset{H}{O}}{CH}{-}\underset{\underset{O}{O}}{CH_2} \qquad (73)$$



$$CH_3\underset{\underset{H}{O}}{CH}{-}\underset{\underset{O}{O}}{CH_2} \rightarrow CH_3CHO + HCHO + OH \qquad (74)$$

This reaction sequence may be important at low temperatures while the direct addition of OH followed by decomposition should become more favored as temperature increases.

2. Propagation and Branching Paths

The propagation process in propene oxidation primarily involves reactions of the allyl radical. At low temperatures, this involves the addition of O_2, forming a peroxy radical, keeping the double bond intact. This radical can then go on to abstract a hydrogen from a source such as the fuel, forming a hydroperoxide:

$$C_3H_5 + O_2 \rightarrow C_3H_5O_2 \qquad (75)$$

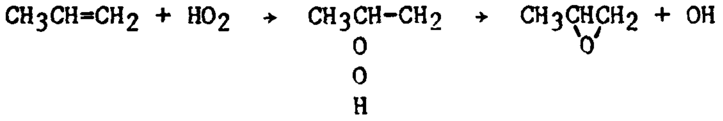
$$C_3H_5O_2 + C_3H_6 \rightarrow C_3H_5OOH + C_3H_5 \qquad (76)$$

Chain branching occurs as the hydroperoxide decomposes, yielding reactive allyloxy and OH radicals:

$$C_3H_5OOH \rightarrow C_3H_5O + OH \qquad (77)$$

The allyloxy formed in Reaction 77 reacts with O_2 and, keeping the double bond intact, leads to the formation of the unsaturated aldehyde - acrolein:

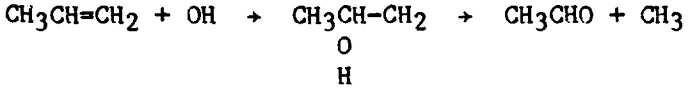
$$C_3H_5O + O_2 \rightarrow CH_2{=}CHCHO + HO_2 \qquad (78)$$



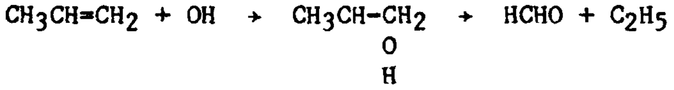
$$CH_3CH{=}CH_2 + HO_2 \rightarrow CH_3\underset{\substack{O\\O\\H}}{CH}{-}CH_2 \rightarrow CH_3\underset{\diagdown O \diagup}{CHCH_2} + OH \qquad (69)$$

This reaction is considered by Baldwin et al. (1981, 1985) to be very important in the low and intermediate temperature oxidation of propene. This reaction sequence is the primary source of propene oxide and also converts HO_2 radicals to very reactive OH radicals.

Reactions involving OH addition to the double bond of the propene are also important and can be used to explain many of the observed products (Baldwin and Walker, 1981):



$$CH_3CH{=}CH_2 + OH \rightarrow CH_3\underset{\substack{O\\H}}{CH}{-}CH_2 \rightarrow CH_3CHO + CH_3 \qquad (70)$$



$$CH_3CH{=}CH_2 + OH \rightarrow CH_3CH{-}\underset{\substack{O\\H}}{CH_2} \rightarrow HCHO + C_2H_5 \qquad (71)$$

These reactions provide paths for the acetaldehyde and formaldehyde formation. Also, the methyl and ethyl radicals formed will lead to the formation of methylperoxy and ethylperoxy radicals at low temperatures:

$$CH_3 + O_2 \rightarrow CH_3O_2 \qquad (30)$$

$$C_2H_5 + O_2 \rightarrow C_2H_5O_2 \qquad (29)$$

and the formation of methane and ethene at intermediate temperatures:

$$CH_3 \xrightarrow{+H} CH_4 \qquad (43)$$

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \qquad (42)$$

At low temperatures the adduct formed from the OH addition in Reaction 71 should not be favored over the one formed in Reaction 70 due to the unselective attack by OH. However, it will be more stable and will tend to break down less readily than that in Reaction 70. Therefore the formation alkenes and alkanes such as ethene and, in particular, methane increase. The amount of carbon monoxide increases with temperature under both lean and rich conditions. Carbon dioxide, however, increases for lean mixtures and decreases for rich mixtures.

C. CHARACTERISTICS OF THE LOW AND INTERMEDIATE TEMPERATURE OXIDATION MECHANISM

1. Initiation and Radical Reactions with the Fuel

At low and intermediate temperatures, the initial step in the oxidation of propene is abstraction of a hydrogen atom by O_2:

$$C_3H_6 + O_2 \rightarrow C_3H_5 + HO_2 \qquad (64)$$

Hydrogen abstraction should occur fairly easily with propene due to the relatively weak C-H bond adjacent to the double bond ($D°_{298}(CH_2{=}CHCH_2{-}H) = 85$ kcal) (Baldwin and Walker, 1973). Reaction 64 results in the formation of the resonance stabilized allyl radical and a hydroperoxyl radical.

As various radicals are formed during the oxidation process, they begin to react with the initial fuel. One way in which they react is to abstract a hydrogen atom. This further increases the pool of allyl radicals:

$$C_3H_6 + HO_2 \rightarrow C_3H_5 + H_2O_2 \qquad (65)$$

$$C_3H_6 + OH \rightarrow C_3H_5 + H_2O \qquad (66)$$

$$C_3H_6 + C_3H_5O_2 \rightarrow C_3H_5 + C_3H_5OOH \qquad (67)$$

$$C_3H_6 + CH_3O_2 \rightarrow C_3H_5 + CH_3OOH \qquad (68)$$

Another way in which radicals react with propene is to add to the double bond. Because of the double bond, free radicals have the tendency to add to it to form a highly energized radical. These resulting adducts can then decompose directly or enter into subsequent reactions. One important radical addition reaction involves the addition of HO_2 to propene:

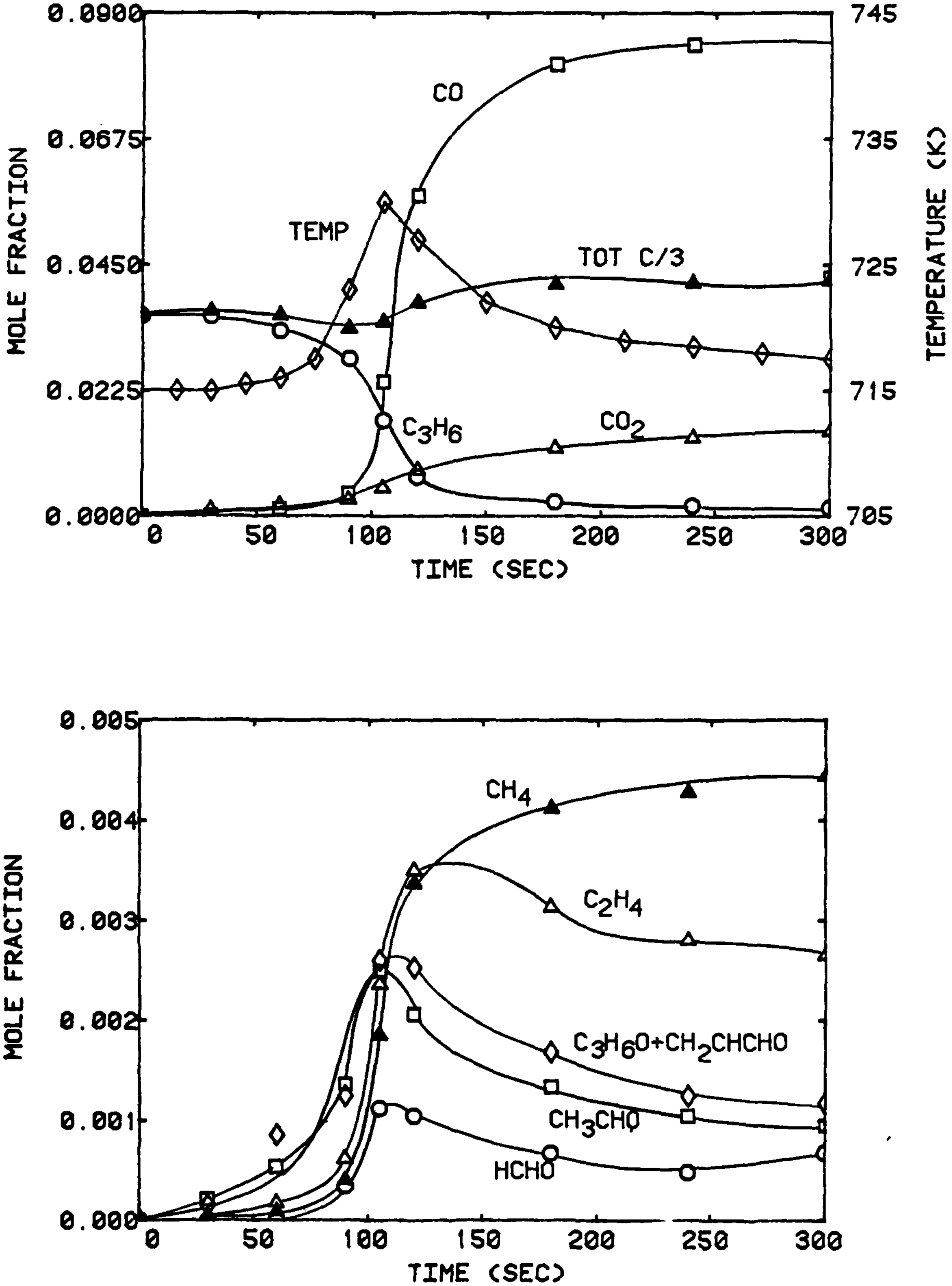


FIG. 30. SPECIES CONCENTRATION AND TEMPERATURE PROFILES FOR C_3H_6/AIR MIXTURES AT ϕ=0.8; Po=600 TORR; To=715 K.

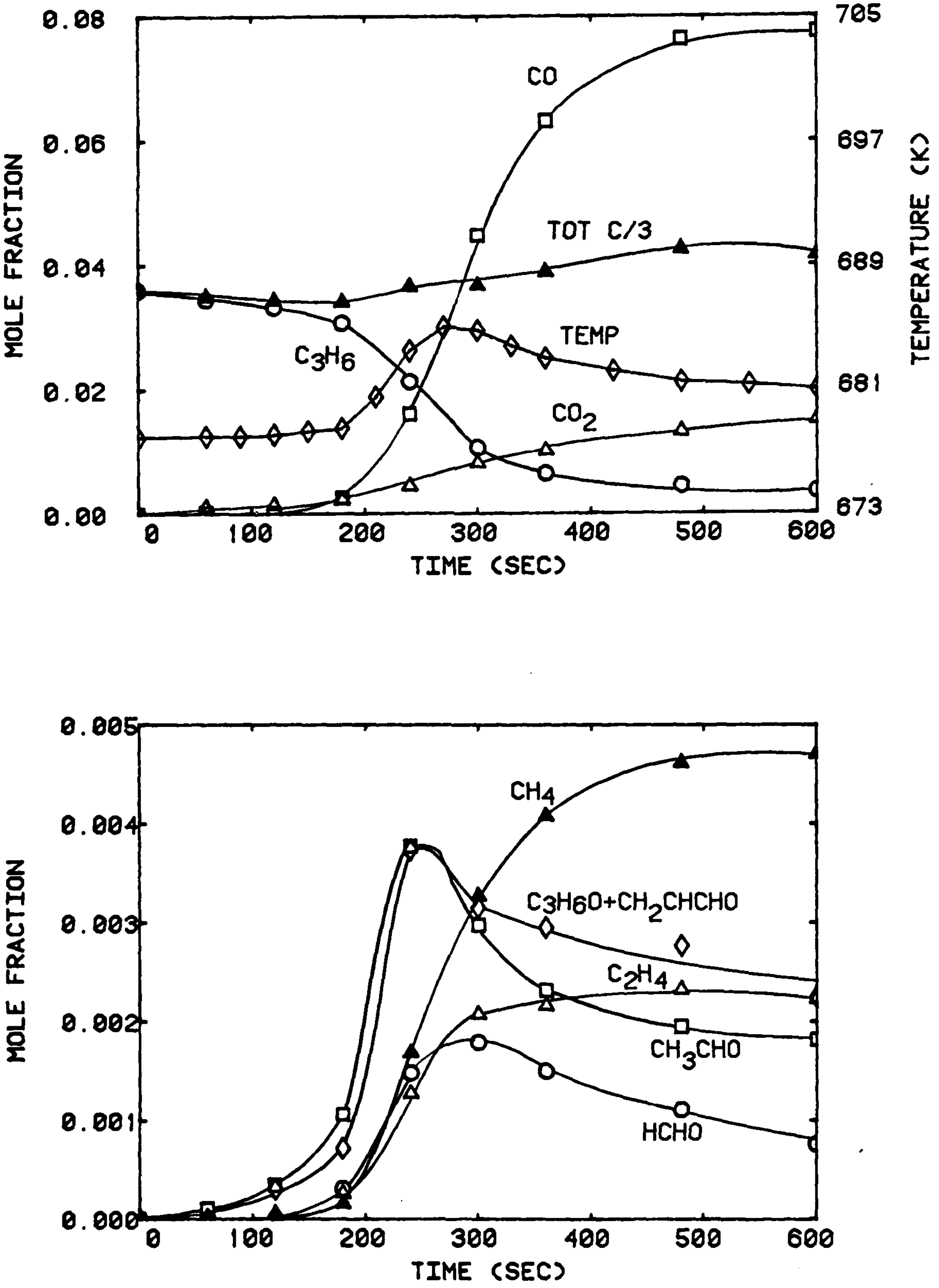


FIG. 29. SPECIES CONCENTRATION AND TEMPERATURE PROFILES FOR C_3H_6/AIR MIXTURES AT $\Phi=0.8$; $P_o=600$ TORR; $T_o=678$ K.

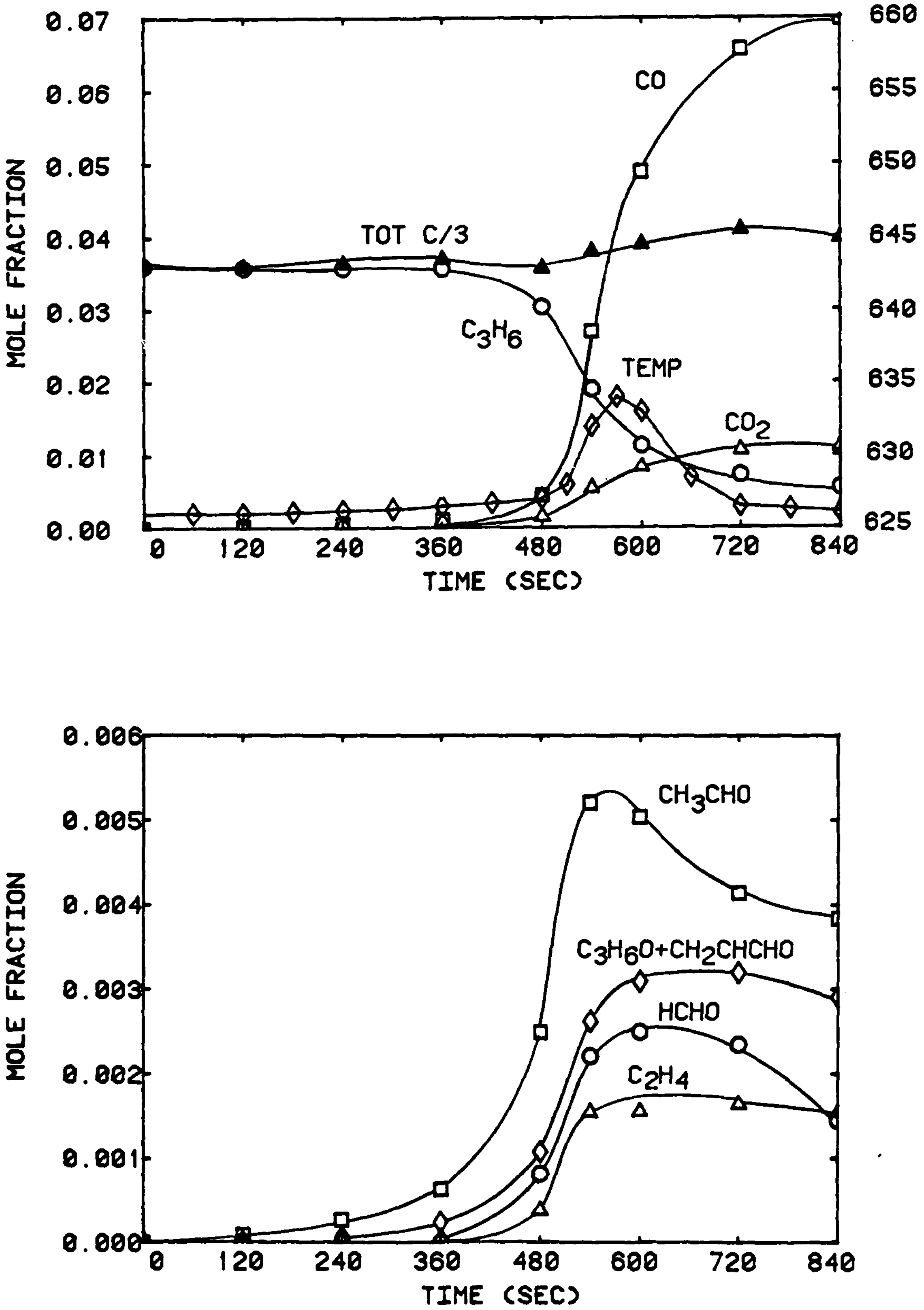


FIG. 28. SPECIES CONCENTRATION AND TEMPERATURE PROFILES FOR C_3H_6/AIR MIXTURES AT $\Phi=0.8$; $P_o=600$ TORR; $T_o=626$ K.

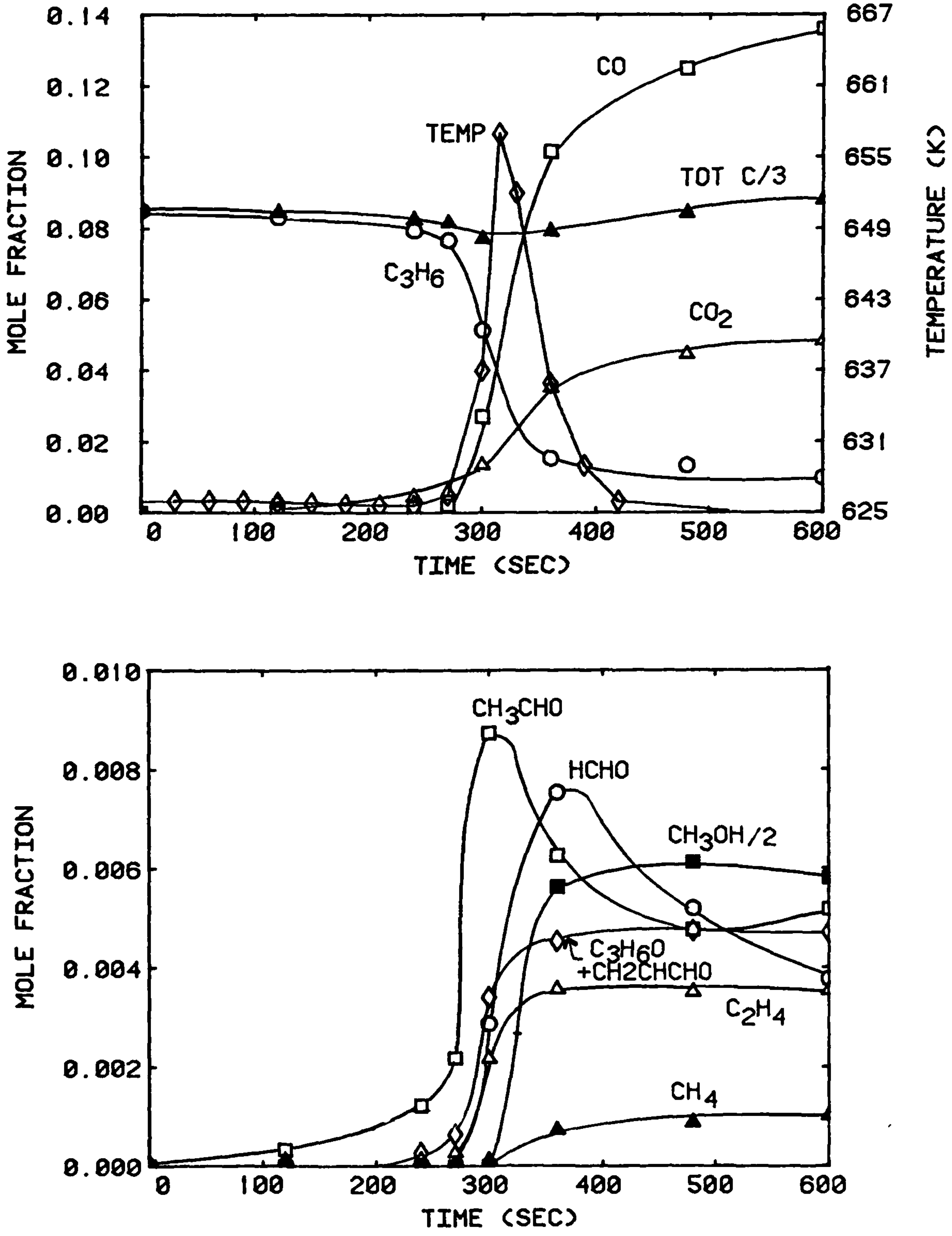


FIG. 27. SPECIES CONCENTRATION AND TEMPERATURE PROFILES FOR C_3H_6/AIR MIXTURES AT $\Phi=2.0$; $P_o=600$ TORR; $T_o=626$ K.

with the results of Nguyen et al. (1970) who have also found that the addition of propene to propane increasingly reduced the importance of the NTC.

As with alkanes such as propane, n-butane, and pentane (Dechaux and Delfosse, 1979), the importance of the NTC of propene increases with decreasing fuel concentration. At $\phi = 0.8$ (Fig. 26), the lobe is greater than that at $\phi = 2.0$, while at $\phi = 3.0$, there is virtually no increase in the induction period, but rather just a leveling off as the temperature passes through the NTC range.

2. Species Measurements

Representative data for the oxidation of propene are presented in the form of species concentration and temperature profiles (Figs. 27-30). The actual data points are shown along with smoothed curves. At each of the experimental conditions, carbon monoxide was found to be the major reaction product. Other major products that were measured include carbon dioxide, ethene, methane, formaldehyde, and acetaldehyde. Propene oxide and acrolein were also present and are given as a single combined quantity since they could not be separated individually by the gas chromatograph at each condition. Trace amounts of acetone, isobutene, and 1,3-butadiene were also detected.

Many of the reaction products were qualitatively and quantitatively affected by the conditions of the experiment. For rich mixtures methanol was present in significant amounts (~1%); whereas, at lean conditions there were no detectable quantities present. Also, at the richest mixture studied ($\phi = 3.0$), small quantities of ethane and acetylene appeared in the products.

Noticeable differences in the reaction products are also apparent as the initial temperature increases across the NTC region. The net yields of oxygenated hydrocarbon species such as formaldehyde, acetaldehyde, and methanol (rich mixtures) decrease. On the other hand, the yields of the lower

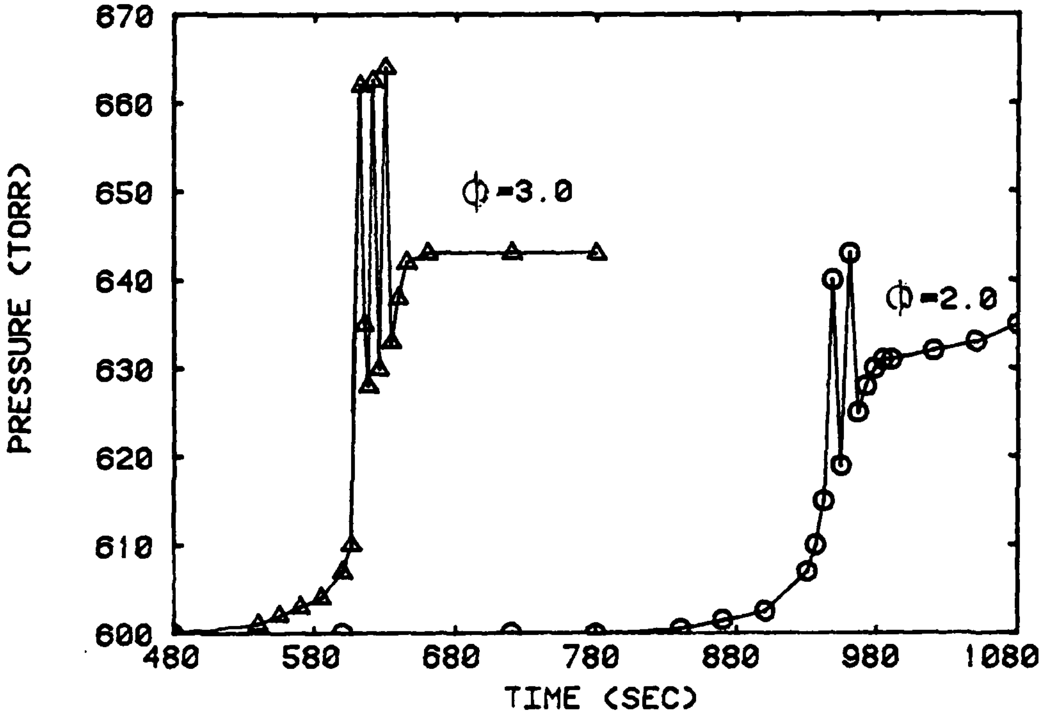


FIG. 25. EFFECT OF EQUIVALENCE RATIO ON THE PRESSURE HISTORIES AND COOL FLAMES FOR C_3H_6/AIR MIXTURES AT To=580 K.

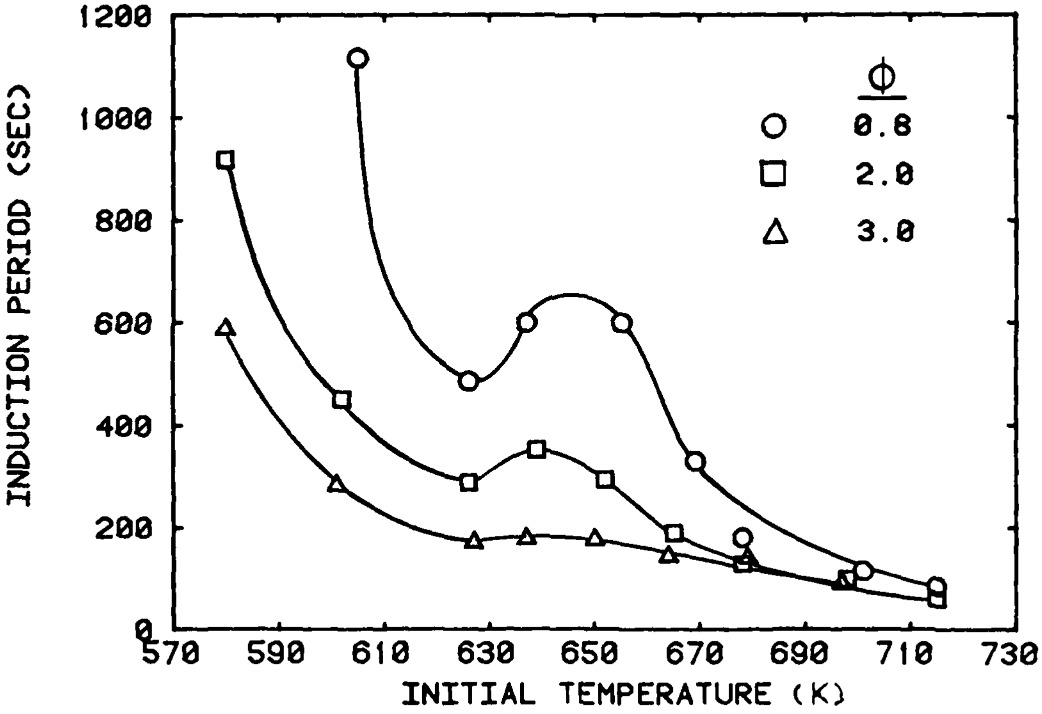


FIG. 26. EFFECT OF INITIAL TEMPERATURE AND EQUIVALENCE RATIO ON THE INDUCTION PERIOD FOR C_3H_6/AIR MIXTURES AT Po=600 TORR.

Cool flames were observed under certain conditions. The occurrence of the cool flames was indicated, as in the propane study, by sharp pressure pulses superimposed on the normal pressure-time curves. At 626 K (Fig. 24), no cool flames were observed for $\phi = 0.8$, while at $\phi = 2.0$ a single, very weak cool flame was noticed. At $\phi = 3.0$, a rather pronounced single cool flame was indicated. In general, cool flames were observed at the lower temperatures in this study (580-626 K) and were more evident for richer mixtures. Also, at certain conditions, multiple cool flames were observed (Fig. 25). Increasing the propene concentration increased both the number and intensity of the cool flames. The cool flame behavior observed here for propene is similar to that found for propane, and, in general, follows the characteristics of the cool flame behavior of most hydrocarbons with the exception of aldehydes (Fish, 1968).

Another similarity between the low temperature oxidation of propene and that of other hydrocarbons is the presence of a region of negative temperature coefficient (NTC). As the initial temperature is increased up to about 630 K, there is a decrease in the induction period and an increase in the maximum overall reaction rate. However, in the narrow range from about 630-650 K, further increase in temperature results in an increase in induction period and a decrease in the maximum reaction rate. Finally, above about 650 K, the induction period again decreases with a corresponding increase in rate. This behavior of induction period is shown in Fig. 26.

From the results of the propane oxidation studies discussed in Section III of this report, the propane exhibited a NTC range of 600-650 K, wider than that obtained for propene (630-650 K). Also, the effect of the NTC of propene was much weaker than that of propane as indicated by the relative prominence of the lobes on the induction period-temperature curves. This is in agreement

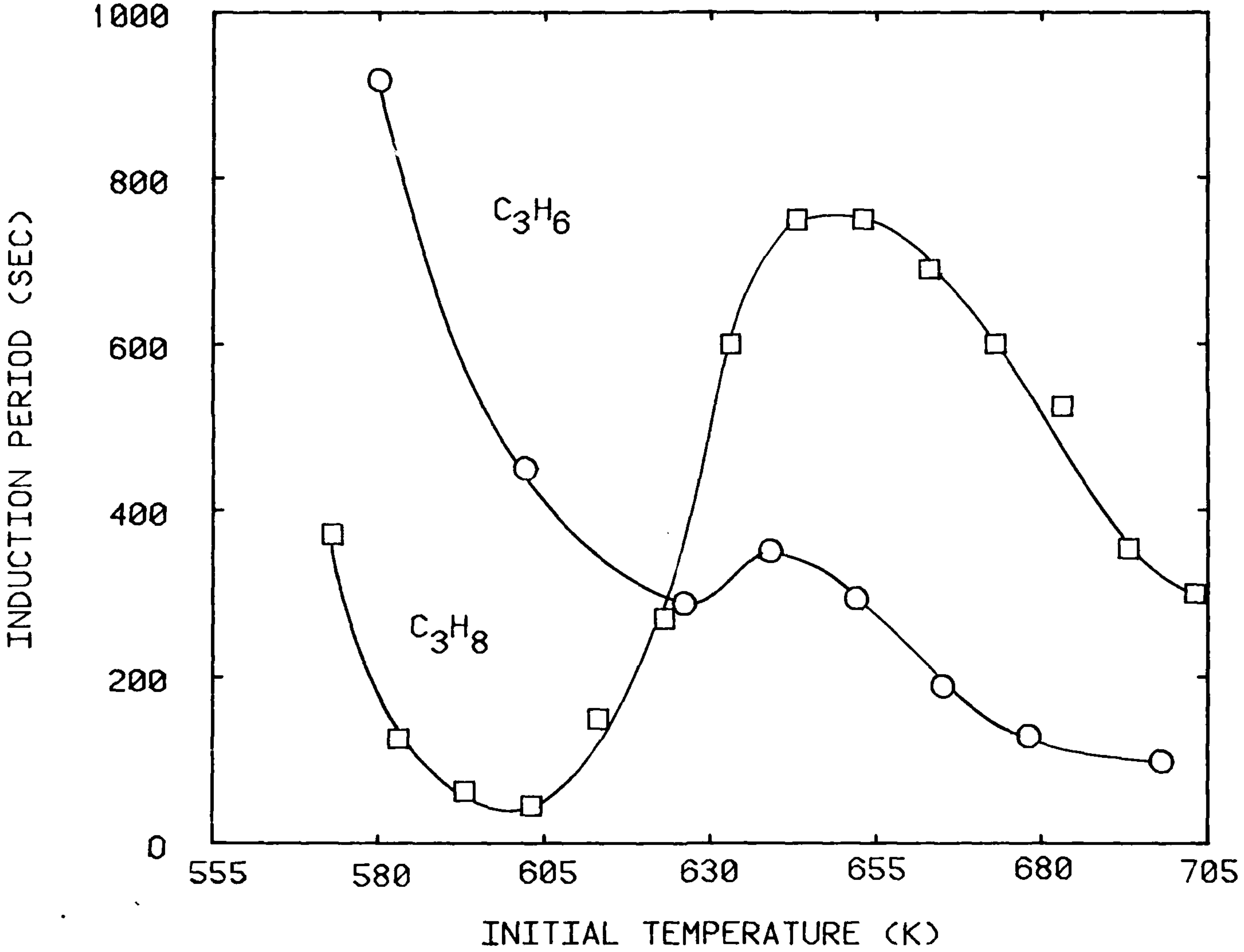


FIG. 31. COMPARISON OF THE NTC REGION FOR C_3H_8 AND C_3H_6; ϕ=2.0; Po=600 TORR.

(shorter induction periods) than the propane. It is necessary to consider each temperature regime separately. In the low temperature regime, propene oxidation is dominated by the radical addition to the double bond of the fuel. Addition of OH or HO_2 radicals to the fuel will result in the formation of less reactive radicals. Because the reactive radicals are replaced by the less reactive radicals, the overall reaction will tend to be slower. In propane oxidation, however, radical addition reactions are not important. Therefore, the overall reaction will tend to be faster as OH and HO_2 can attack the fuel directly.

In addition, the initial main propagating radical in propene oxidation is the stable allyl radical while in propane oxidation it is the more reactive alkyl radical. Thus, in the low temperature regime, propane is more reactive and has shorter induction periods than propene.

On the other hand, in the intermediate temperature or post NTC regime, propene is more reactive than propane, as it exhibits shorter induction periods. Salooja (1968) concluded that, in this temperature range, the factor controlling the reactivity of these fuels is the nature of the bonds of each fuel molecule. The higher reactivity of propene is attributed to the weaker C-H bond strength in the α position to the double bond of propene as compared to any of the C-H bonds in propane. So with propene, initial hydrogen abstraction occurs more easily which allows it to undergo chain reactions more readily, thus making it more reactive.

From these comparisons, the effect of the presence of propene in the oxidation of propane can be determined. In the low temperature regime, propene would tend to inhibit propane oxidation, while in the intermediate temperature regime, the presence of the propene would tend to enhance propane oxidation and promote autoignition. This latter effect has practical significance since alkenes tend to be knock promoters or, more importantly for diesel fuels, alkene additives are useful as cetane boosters.

D. CHEMICAL KINETIC MODELING

The experimental results from Part B were used to model the low and intermediate temperature oxidation of propene. Two approaches for the chemical kinetic modeling of this fuel were considered. The first approach would have been to formulate a mechanism based solely upon the experimental results obtained from this work. This would have involved obtaining Arrhenius parameters (preexponential constant and activation energy) for the individual propene reactions listed in Part C of this section. In addition, in order to accurately model the propene, submechanisms for the various intermediates such as acetaldehyde, formaldehyde, ethene, carbon monoxide, and hydrogen would have to be included. The result of such an effort would be very useful for predicting the oxidation chemistry of propene. However, its application would be limited to the conditions of these experiments (low and intermediate temperatures and low pressures).

As mentioned earlier in this report, for a chemical kinetic mechanism to be effective for use in the modeling of actual combustion devices, the mechanism should be comprehensive. That is, it should be applicable simultaneously to a wide range of combustion regimes. Thus, in keeping with this concept, a second approach to the chemical modeling was adopted. With this approach, instead of developing a separate model, it was decided to use the experimental results to modify and extend an existing model. The model used for this purpose was the one developed by Westbrook and Pitz (1984). This chemical kinetic mechanism was developed primarily for high temperature ($T>1000$ K) oxidation and pyrolysis of propene; it was formulated and validated using data from high temperature experimental systems (shock tubes, flow reactors, and flames). However, the model still needed to be extended to lower temperatures in order for it to be used to accurately predict auto-ignition. This was made possible by the experimental results from the present study.

This modeling work was a collaborative effort with the original developers of the mechanism, Charles K. Westbrook and William J. Pitz of Lawrence Livermore National Laboratory. Although this work is still continuing and the mechanism is still being refined, significant progress has been made. Therefore, the current status of the work at the time of this report will be outlined here along with the anticipated future directions.

It was shown that there are significant differences in the oxidation chemistry of propene between low and high temperatures. Therefore, the first step in the modeling was to attempt to predict the low and intermediate temperature results using the existing high temperature model. This was done to determine which portions of the model needed modification. The computer modeling was carried out using the HCT code (Lund, 1978), which solves the coupled chemical kinetics and energy equations.

As initially expected, the numerical predictions and the experimental data were not in very good agreement. For example, the model underpredicted the amount of acetaldehyde formed by a factor of ten, while the formaldehyde was overpredicted by about a factor of four. Also, the predicted induction period was much too short.

It was attempted to eliminate these differences by incorporating some of the reactions listed in Part C of this section into the mechanism; that is, reactions believed to be important in the low and intermediate temperature regimes. For example, Reaction 70 was added to give an additional path for the formation of acetaldehyde. Arrhenius parameters for the added reactions were obtained from the literature or estimated. These parameters were then adjusted within acceptable ranges to provide the best possible agreement between numerical and experimenatl results.

Comparisons of the experimental and computed results for one case

(T_0=715 K, P_0=600 torr, and ϕ=0.8) are presented in Figs. 32-35. The experimental data are represented by the open symbols and the computed species concentrations, temperature, and pressure profiles are indicated by solid curves. The computed propene consumption and carbon monoxide formation profiles are generally in good agreement with the experimental data (Fig. 32). The model correctly predicts the S-shaped profiles with a well defined induction period. The predicted reaction rate is slightly faster in the initial stages of the reaction and slightly slower in the final stages.

The computed acetaldehyde and ethene profiles are shown in Figs. 33 and 34, respectively. Although the general trends are similar, the predicted maximum net yield of acetaldehyde is still about 30% too low while that of the ethene is about 40% too high. However, the times at which the maxima occur are in good agreement with the measured data.

Finally, the computed temperature and pressure profiles are in fairly good agreement with the measured results (Fig. 35). The predicted and measured results basically show the same trends. The maximum and final temperatures are accurately predicted although the predicted maximum temperature lags slightly behind that of the measured value. Also the predicted final pressure is slightly higher than that measured.

Despite these differences, it can be seen from these results that the current modified version of the model, in general, predicts the experimental results fairly well. However, as stated, this modeling work is still in progress and the mechanism is in the process of being refined in order to better predict the low and intermediate temperature experimental data. For example, one important goal of this modeling activity is to obtain a better prediction of the induction period. From the results thus far, the computed reaction rate at the initial stage of the reaction is still slightly faster than the experimental rate. One way which is being considered to reduce

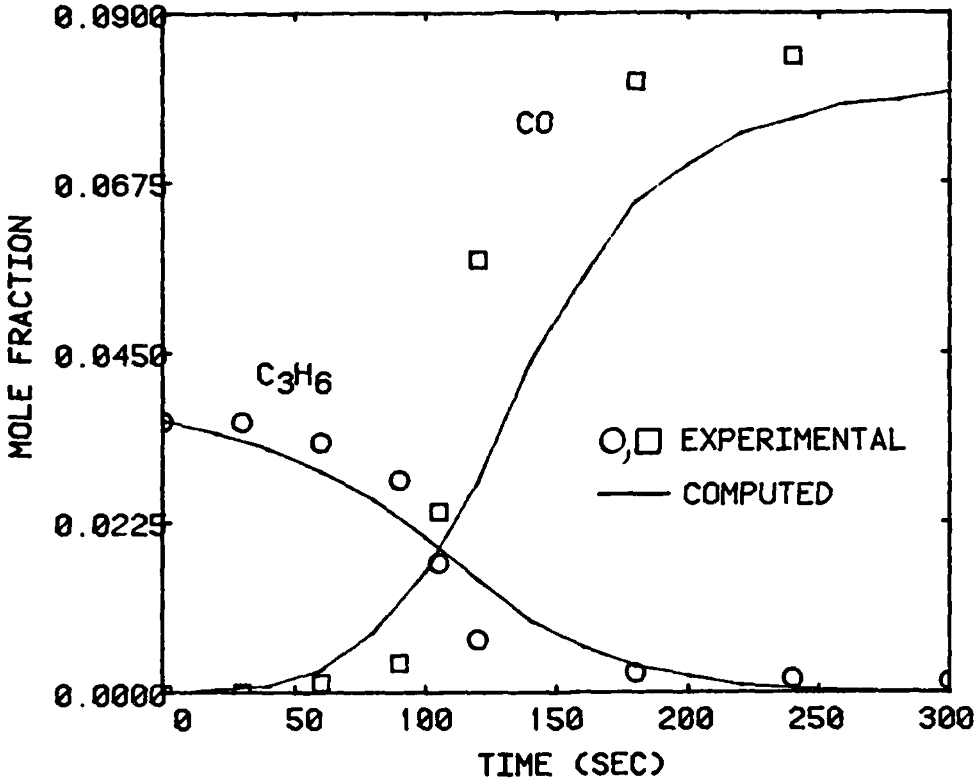


FIG. 32. COMPUTED AND EXPERIMENTAL CONCENTRATION-TIME PROFILES FOR C_3H_6 AND CO; ϕ=0.8; Po=600 TORR; To=715 K.

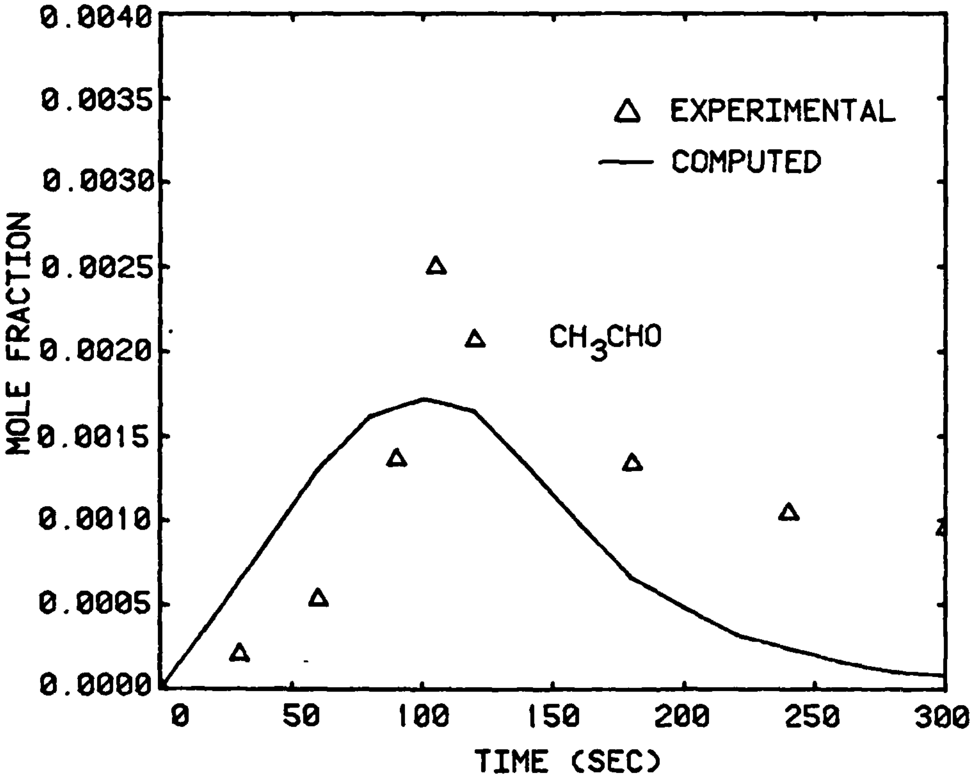


FIG. 33. COMPUTED AND EXPERIMENTAL CONCENTRATION-TIME PROFILES FOR CH_3CHO FORMED IN THE OXIDATION OF C_3H_6/AIR AT ϕ=0.8; Po=600 TORR; To=715 K.

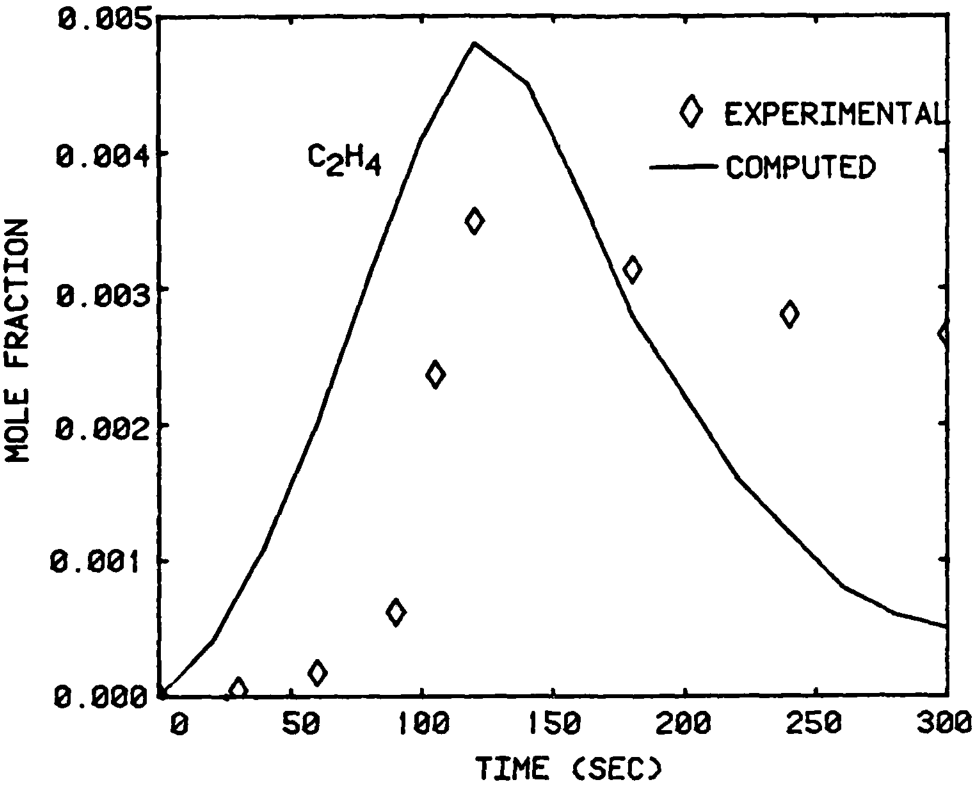


FIG. 34. COMPUTED AND EXPERIMENTAL CONCENTRATION-TIME PROFILES FOR C_2H_4 FORMED IN THE OXIDATION OF C_3H_6/AIR AT Φ=0.8; P_o=600 TORR; T_o=715 K.

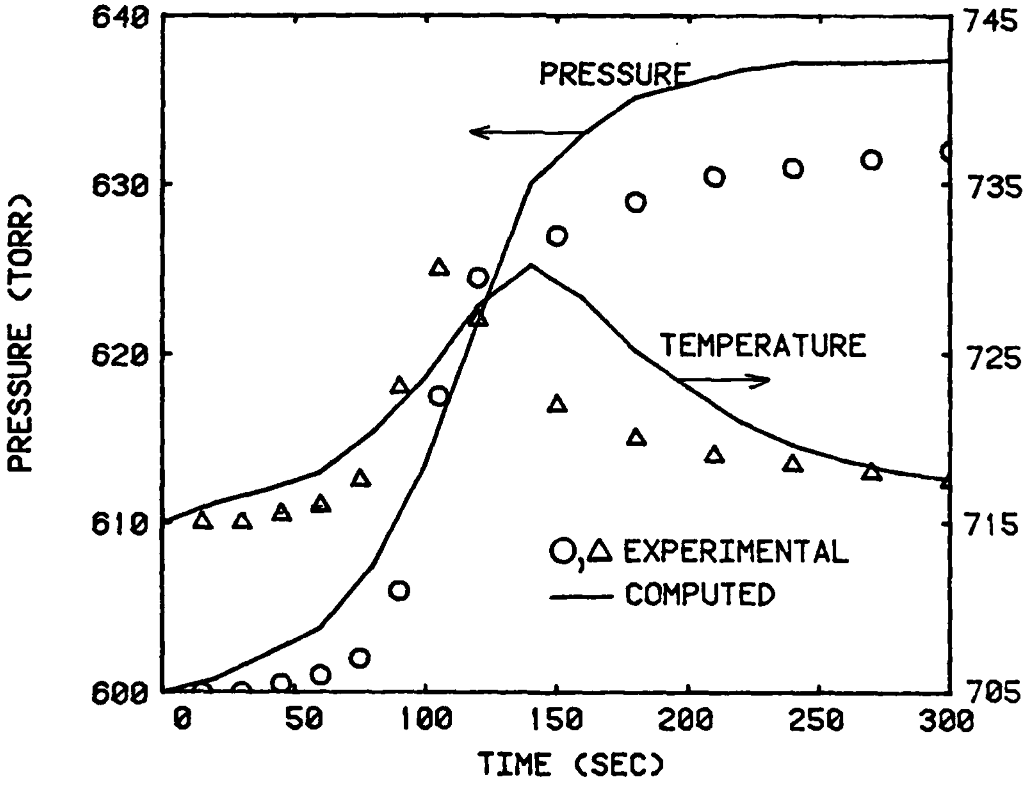


FIG. 35. COMPUTED AND EXPERIMENTAL PRESSURE AND TEMPERATURE HISTORIES FOR THE OXIDATION OF C_3H_6/AIR AT Φ=0.8.

the discrepancy involves adding heterogeneous termination reactions to the mechanism. These reactions are known to occur in actual systems and they involve the destruction of propagating radicals such as OH and HO_2 on surfaces, thereby slowing the reaction. Thus, this modification and others are being considered in order to "fine tune" the mechanism. Once this is accomplished, the propene mechanism can be incorporated as a submechanism into the propane oxidation mechanism.

V. IGNITION STUDIES OF LIQUID FUELS AND LIQUID FUEL MIXTURES

A. INTRODUCTION

Actual full-boiling range fuels; such as gasoline and diesel fuel are comprised of complex multicomponent mixtures of liquid hydrocarbons. The majority of these components are of relatively high molecular weight, with carbon numbers in the range C_8-C_{12}. Determining the detailed autoignition chemistry of these fuels is a difficult task due to the interaction of the various classes of fuel components and the numerous product species which result from the breakdown of heavy fuels. The best approach is to isolate and study single-component hydrocarbons of higher molecular weight and then extend it to simple mixtures of pure fuels to determine the combined effects on the ignition behavior.

Early studies on the ignition behavior were primarily concerned with relatively low molecular weight pure hydrocarbons with carbon numbers in the range C_3-C_8. These studies were concerned mainly with cool flames and two-stage ignition (Knox and Norrish, 1954; Bonner and Tipper, 1965; Hughes and Simmons, 1970; Hughes and Prodhan, 1973; Kutcha and Martindill, 1967; Barat et al., 1972; Johnson et al., 1954; and Affleck and Fish, 1967). The work on ignition behavior was extended to decane by Cullis and Foster (1977, 1982), who obtained a correlation with the thermal ignition theory of Frank-Kamenetskii and determined experimentally some of the detailed chemistry of decane oxidation. In another study, Kadota et al. (1976) obtained results on the general ignition characteristics of pure high carbon number fuels and, in particular, developed expressions for the ignition delay of dodecane and hexadecane at high pressure. Spadaccini and TeVelde (1982) obtained an empirical expression for the ignition delay of cetane and actual fuels such as Jet A, JP-4, No. 2 Diesel and the ERBS (experimental referee broad specification) fuel.

Some studies have been made on the ignition characteristics of binary mixtures of pure hydrocarbons. Most of the components had carbon numbers in the range C_6-C_8 (Ma and Moore, 1966; and Cullis et al., 1969). Salooja (1968) reported on the ignition behavior of a number of binary mixtures composed of both aromatic and aliphatic components in the C_6-C_8 range. Brezinsky and Dryer (1985) presented an explanation of the inhibiting effect of branched alkanes from a study of the oxidation of isobutene/n-octane mixtures. Cullis and Foster (1974) demonstrated the way in which the separate components of a mixture affect cool flames and two-stage ignition by examining the effects of the addition of 2,2,5-trimethylhexane to decane.

Much of the work on preignition and ignition behavior has involved gas phase oxidation in static systems. This was the case with the work on propane and propene, described in the two preceeding sections. Both of these gaseous fuels were first premixed with oxidizer in a separate mixing vessel. When liquid fuels are used, they are usually first prevaporized and then premixed with the oxidizer before being admitted to a heated reaction vessel. This method is satisfactory for low molecular weight fuels which vaporize at relatively low temperatures. However, higher molecular weight fuels are of lower volatility and are, in general, more reactive, as most have lower activation energies for their initiation reactions. Thus, there is the possibility of significant reactions occuring during the evaporation or mixing stages. An additional problem has been identified by Barnard and Harwood (1974), who have shown that errors in ignition data may occur if the reaction becomes exothermic before temperature equilibration is achieved following admission of the reactants into the heated reaction vessel. Cullis et al. (1981) have overcome this problem by employing a different technique in which the fuel is sprayed directly into the reaction vessel, which has been prefilled with oxidizer and preheated to the reaction temperature.

This experimental technique was adopted in this research project to study the ignition characteristics of liquid fuels.

This section presents experimental results of studies which were made of the ignition characteristics of dodecane. In addition, the effects of combining this fuel in a binary mixture with the aromatic fuel tetralin (tetrahydronaphthalene) were examined. These two fuels were selected for study because they are representative of major components of diesel fuel.

B. EXPERIMENTAL RESULTS FOR DODECANE

1. Induction Period Analysis

Figure 36 shows four pressure-time profiles for the reaction of dodecane in air at 523 K. At the instant of injection, the pressure drops slightly due to the cooling effect as the fuel enters the reaction vessel. This is followed by an increase in pressure due to the vaporization of the fuel. Slow combustion was observed at an initial pressure of 70 torr (Fig. 36a), with only a 3 torr increase in pressure. As the initial pressure is increased, a single cool flame is observed as indicated by the pressure pulse (Fig. 36b). Two cool flames are observed at an initial pressure 390 torr (Fig. 36c) and as the initial pressure is further increased, a two-stage ignition is indicated by a cool flame followed by hot ignition (Fig. 36d).

The induction period preceding the first cool flame is taken as the time from injection to the beginning of the pressure rise. This time includes the vaporization time, which is small compared with the overall induction period for most of the conditions used in this work. Also, it has been shown earlier that the rate of formation of a homogeneous mixture is much faster than the rate of vaporization (Cullis *et al.*, 1981). Thus, in these studies it is assumed that the preignition kinetics are rate controlling.

The effect of initial pressure on the induction period preceding the

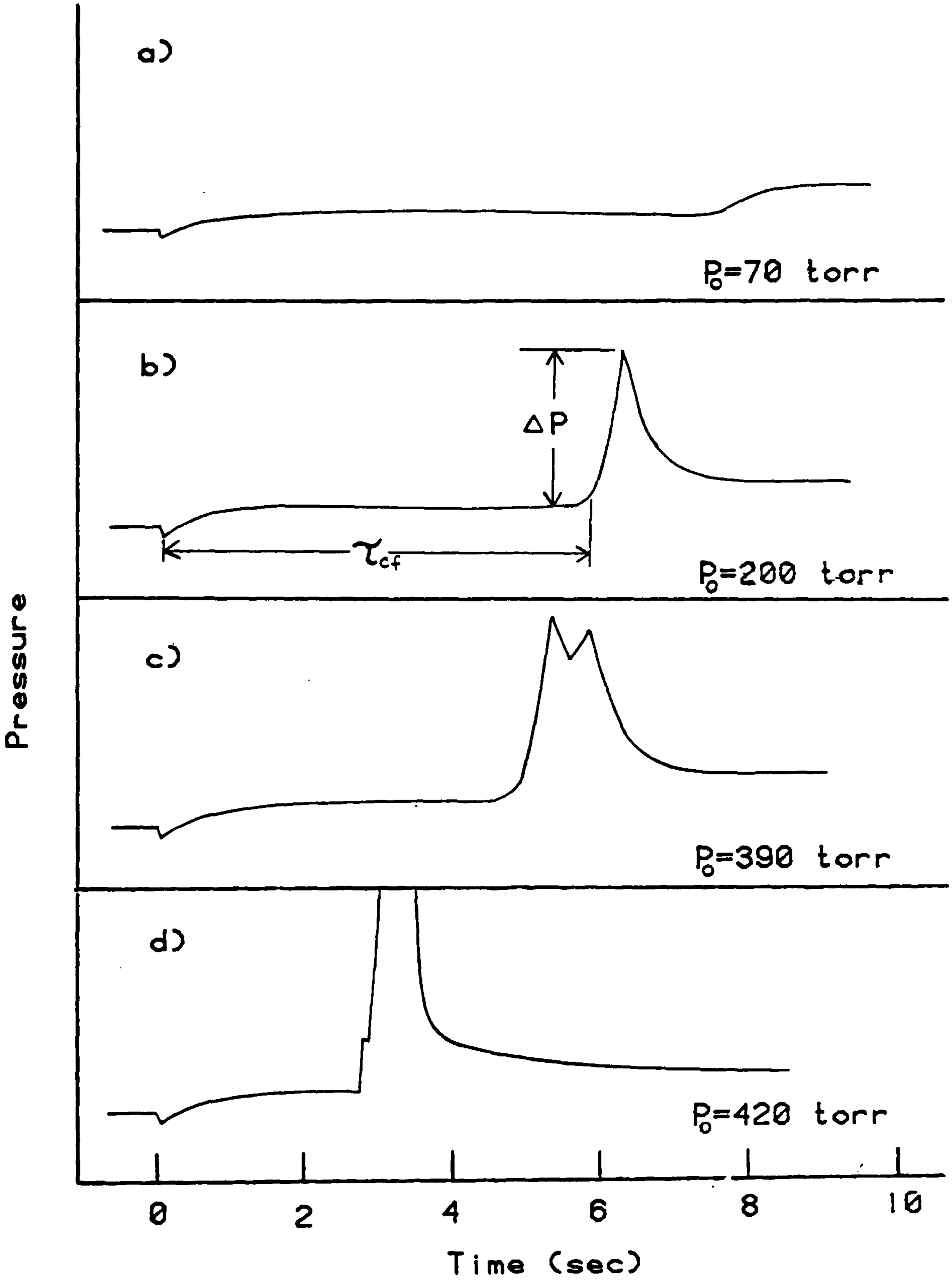


FIG. 36. PRESSURE HISTORIES FOR THE OXIDATION OF $C_{12}H_{26}$/AIR MIXTURES AT ϕ=1.0; To=523 K.

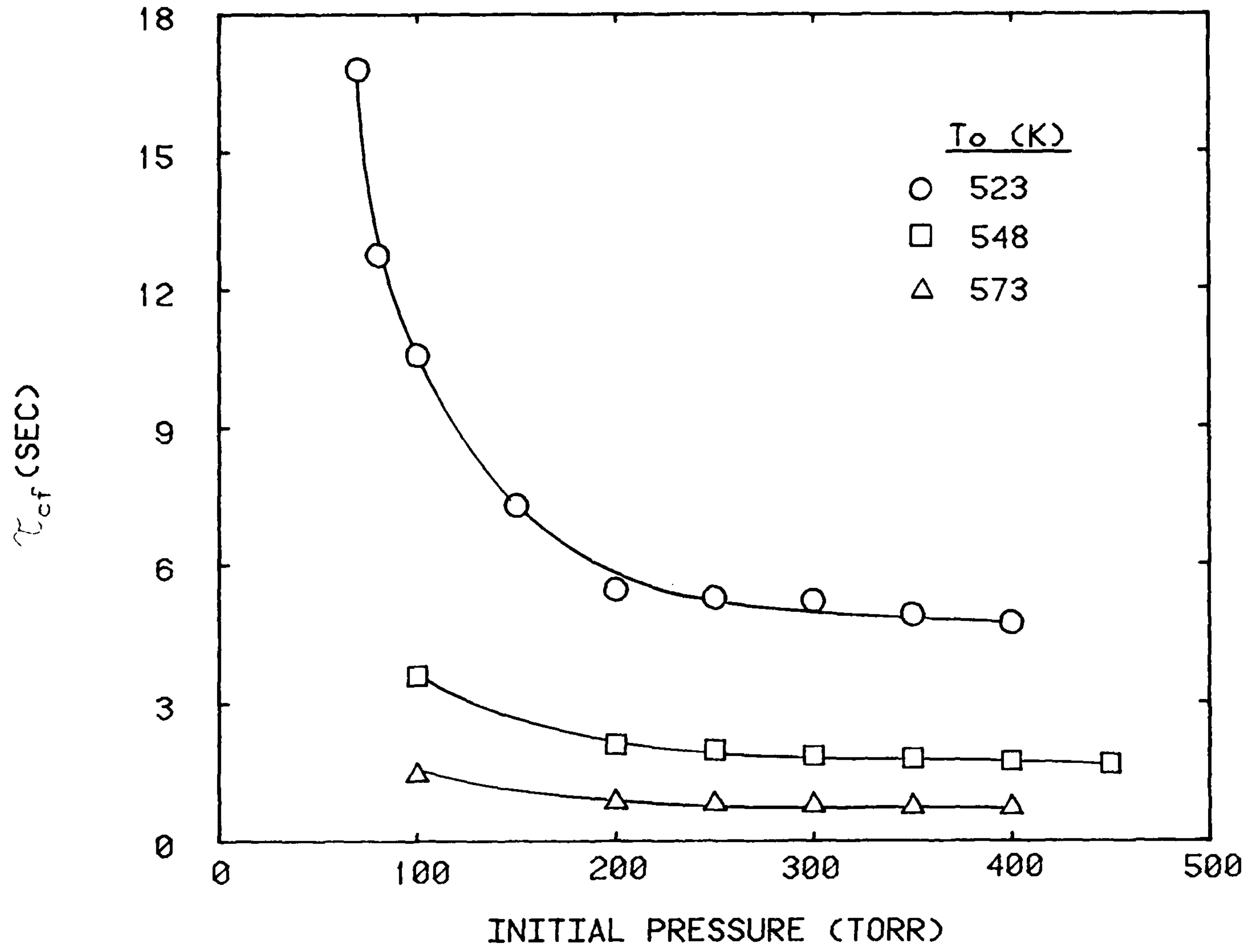


FIG. 37. EFFECT OF INITIAL PRESSURE ON THE INDUCTION PERIOD PRECEDING THE FIRST COOL FLAME FOR $C_{12}H_{26}$/AIR MIXTURES AT $\phi=1.0$.

first cool flame, τ_{cf}, is shown for various initial temperatures in Fig. 37. It has been determined in earlier work that for a given temperature and fuel composition this induction period can best be expressed by an equation of the form

$$\tau_{cf} = kP_o^{-n} + c$$

where P_o is the initial pressure and k, n, and c are parameters which are temperature dependent (Fish, 1966). The value of c is believed to correspond to that induction time at the transition from the cool flame region to the two-stage ignition region (Cullis and Foster, 1974). The values of k and n have been shown to have a cyclic variation with temperature (Affleck and Fish, 1967; Cullis and Foster, 1974; Fish, 1966; and McKay, 1977). Some values of these parameters obtained in this study, given in Table IV confirm this pattern.

TABLE IV. Values for the Initial Pressure Parameters k, n and c, for Correlating the Cool Flame Induction Period.

T (K)	k	n	c
523	80866	2.076	4.487
533	621	1.157	3.561
548	12229	1.893	1.595
573	30524	2.310	0.707

In addition, it has been shown that the dependence of induction period on initial temperature can be represented by an equation of the form

$$\tau_{cf} \sim \exp\ (E_a/RT_o)$$

where E_a is the apparent overall activation energy for the preignition reactions, R is the universal gas constant and T_o is the initial temperature of the reactants (Cullis and Foster, 1977).

The apparent overall activation energy was determined from the slope of a

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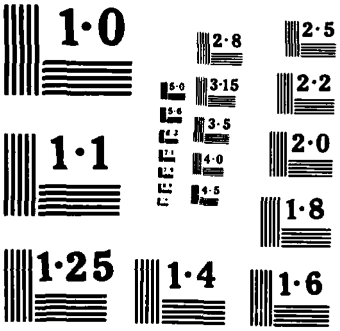

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least squares fit of ln τ_{cf} against $1/T_o$ (Figs. 38 and 39) and was found to be 97.1 kJ/mol (23.1 kcal/mol). This value is constant over the temperature range examined in this work. However, a shift in the slope has been shown for many lower hydrocarbons (Affleck and Fish, 1967; Cullis and Foster, 1977; Fish, 1966; and Bastow and Cullis, 1974) and attributed to a change in the nature of the chain branching reactions. Thus, it is anticipated that a shift to a lower activation energy is likely to occur at higher temperatures.

From Fig. 38 it can be seen that the slope and, therefore, the apparent activation energy remain essentially constant as the initial pressure changes. The effect of initial pressure is only seen in the pre-exponential factor, as indicated by the different intercepts, and may be due to the manner in which the surface affects the initiation and termination reactions. In Fig. 39 the data for three different equivalence ratios fall on a single line. This may suggest that E_a is independent of equivalence ratio; however, no conclusions can be made about the dependence on either the fuel or oxygen individually, since in these studies both were varied simultaneously.

2. Pressure Effects on Cool Flame Intensity

The effect of initial pressure on the pressure rise accompanying the first cool flame has been shown for a number of alkanes (Cullis and Foster 1974; Fish, 1966; and McKay, 1977) to follow the form

$$\Delta P_{cf} = AP_o^m$$

where A and m are constants for a given fuel composition. Figure 40 shows plots of cool flame pressure rise against initial pressure for varying initial temperatures. It can be seen that the pressure rise increases with increasing initial pressure. From the data, an average value of m was found to be 1.37. This value is comparable with values obtained for other hydrocarbons (Table V).

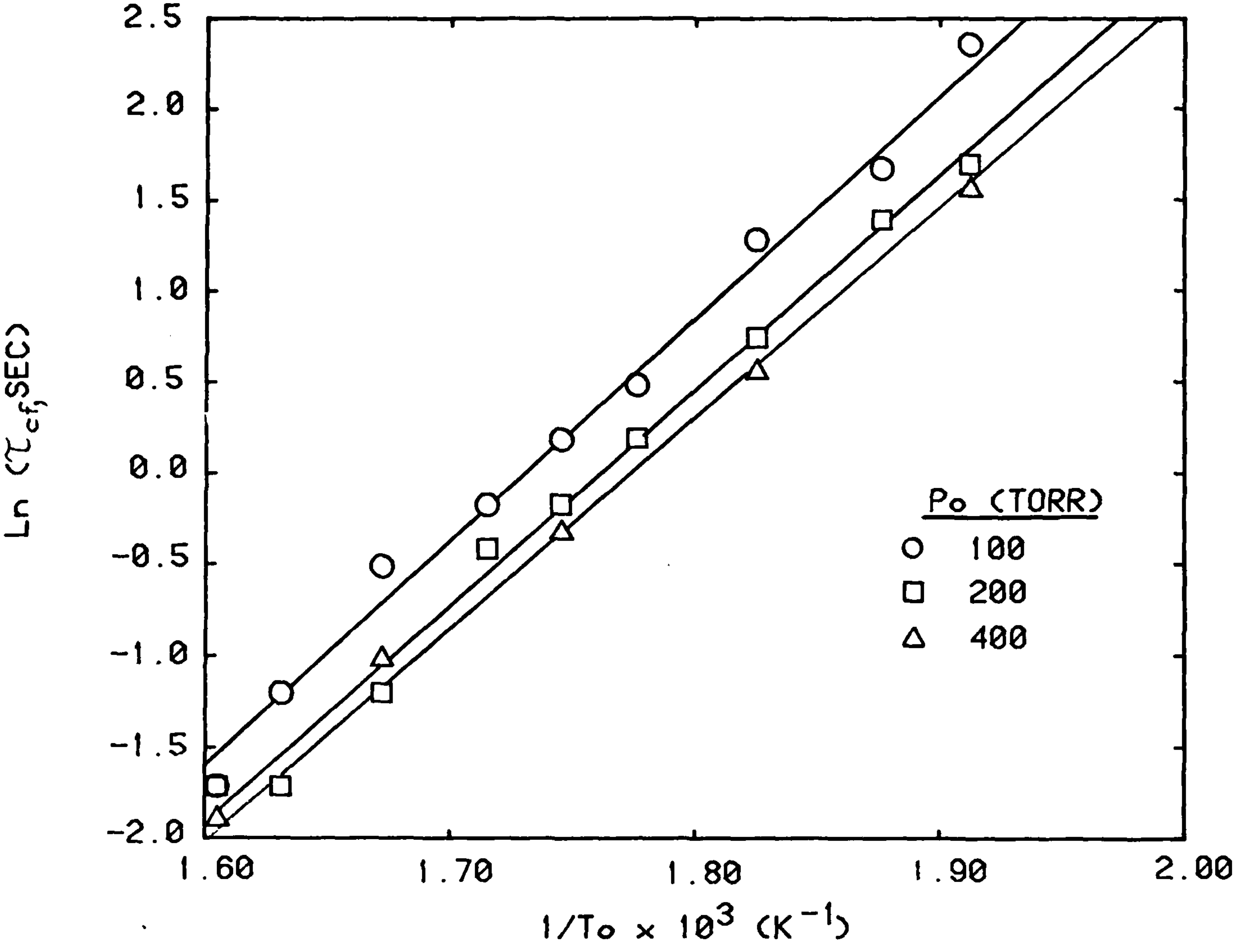

FIG. 38. EFFECT OF INITIAL TEMPERATURE ON THE INDUCTION PERIOD PRECEDING THE FIRST COOL FLAME FOR $C_{12}H_{26}$/AIR MIXTURES AT ϕ=1.0.

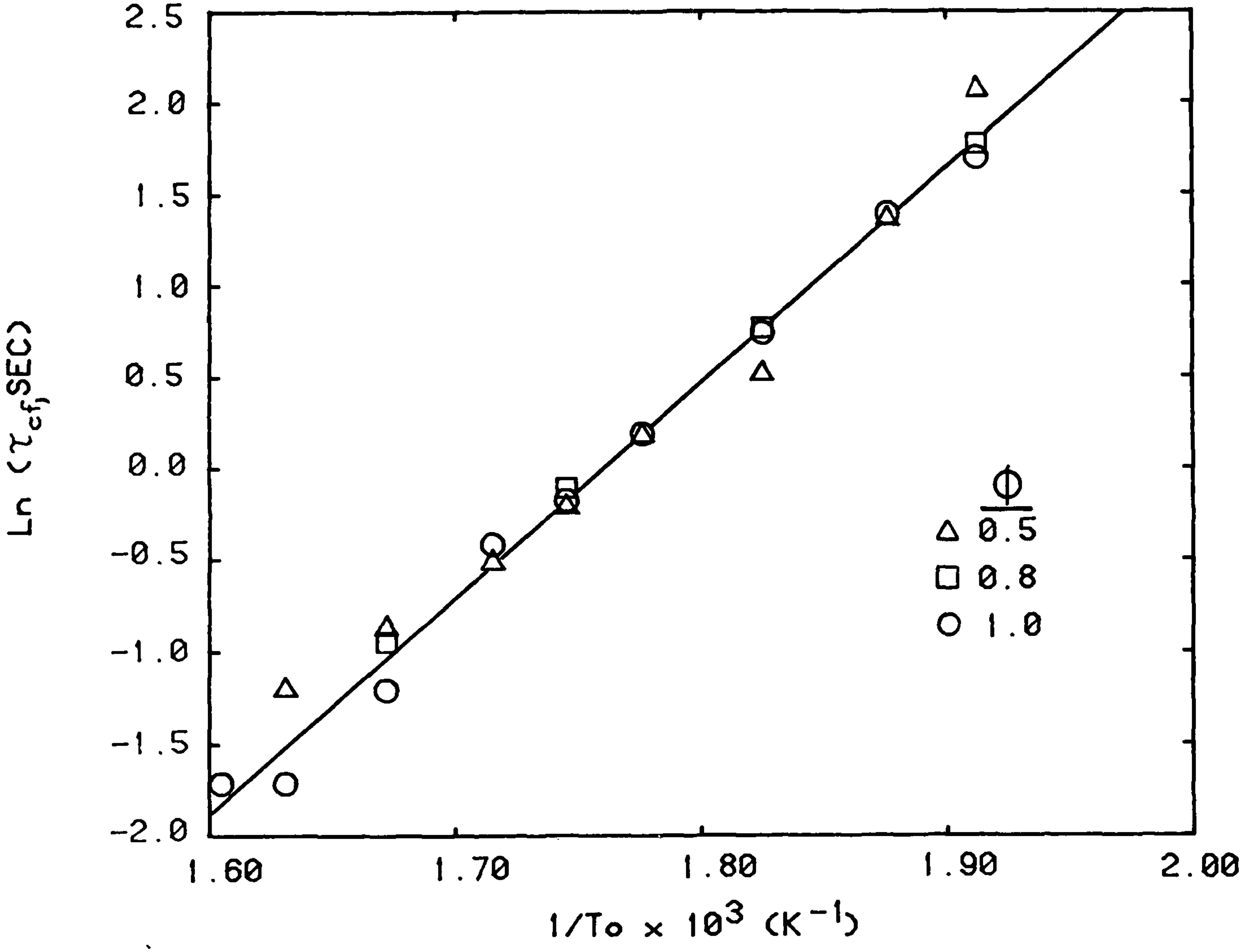

FIG. 39. EFFECT OF INITIAL TEMPERATURE ON THE INDUCTION PERIOD PRECEDING THE FIRST COOL FLAME FOR $C_{12}H_{26}$/AIR MIXTURES AT Po=200 TORR.

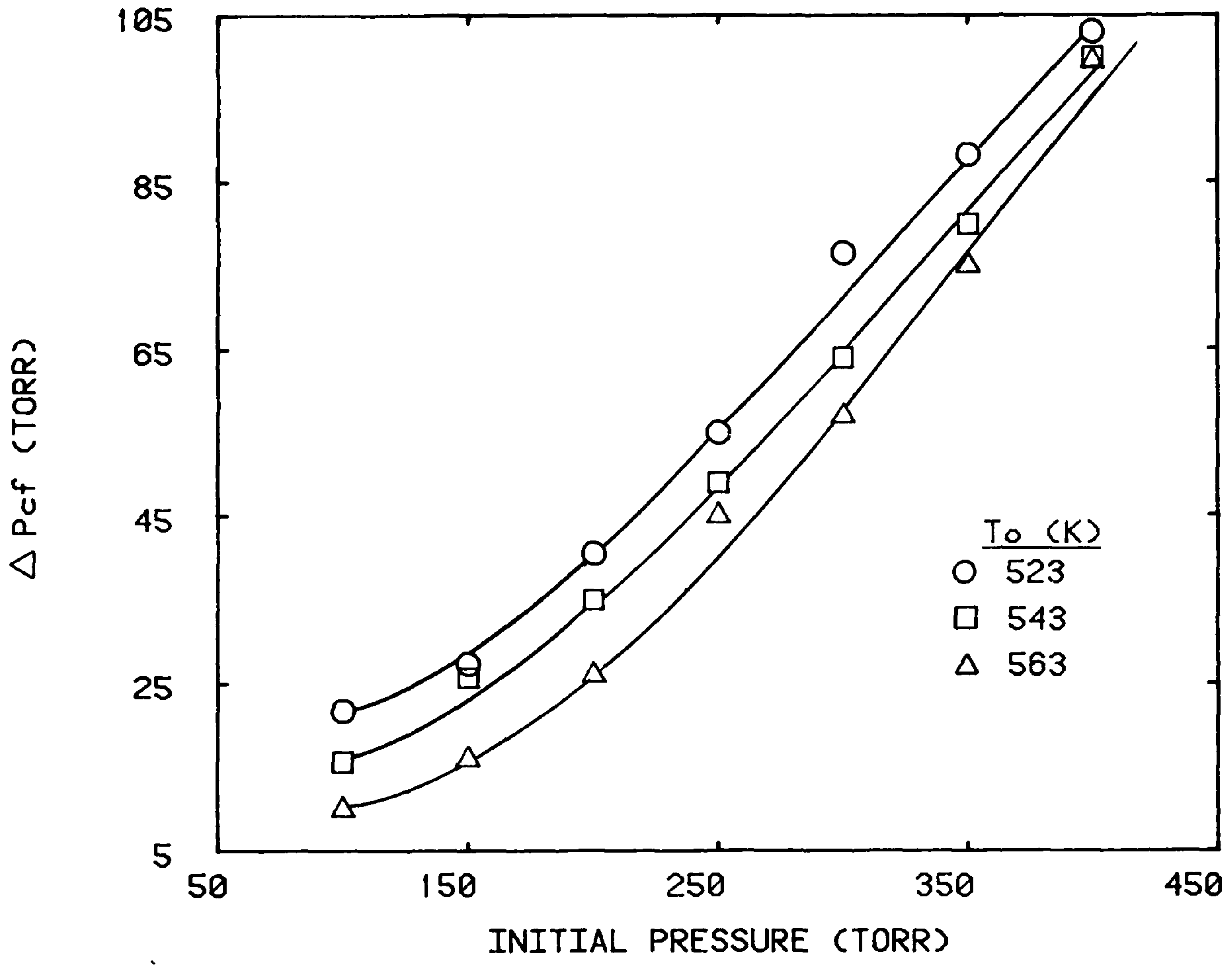

FIG. 40. EFFECT OF INITIAL PRESSURE ON THE MAXIMUM PRESSURE OF THE FIRST COOL FLAME FOR $C_{12}H_{26}$/AIR MIXTURES AT $\phi=1.0$.

TABLE V. Values for the Initial Pressure Exponent, m, For Correlating First Cool Flame Pressure Rise

Fuel	m
Dodecane (This work)	1.37
2,3-Dimethylbutane	2.60 *
2-Methylpentane	1.65 *
Iso-octane	1.50 *
Neopentane	1.00 *

* From McKay (1977).

3. Species Measurements

Species measurements were made on the oxidation of dodecane in air. The oxidation of this fuel is complex, producing large numbers of intermediate and product species. Because of this, only semi-quantitative/qualitative analyses were possible. This was done by using the chromatographic peak profiling technique to process and interpret the chromatographic data.

The peak profiling technque was originally developed to facilitate the analysis of complicated chromatograms. Instead of separating, identifying, and quantifying each species in a sample, with this technique, which is basically a pattern analysis method, the chromatograms are treated as a fingerprint of the sample. The individual peak areas from the chromatograms, which are representative of the quantity of each species, are plotted as spikes against the retention time. The height of each spike is indicative of the amount of that compound present in the particular sample. The retention time, which is the time it takes for a given species to elute from the GC column, is essentially an identification indicator.

The technique allows differences between the chromatograms to be correlated to physical differences between the samples (Jeltes, 1974; Sarv, 1981). It also allows for the identification of important peaks (species) which could be isolated for more detailed analysis such as with GCMS (gas chromatography-mass spectroscopy). In addition, the technique could be used to establish correlations with operating conditions, fuel properties, and other system variables without detailed identification of each peak component.

Chromatographic peak profiles for the oxidation of dodecane are presented in Fig. 41. Samples were obtained at five different times during the course of the reaction. Each profile represents the "fingerprint" of the sample at a particular point in the reaction. Peak profiles are also given for C_5-C_{12} alkane standards for the purpose of making a qualitative comparison with the sample profiles.

As the reaction progresses from 3 seconds, the number of intermediate species formed increases until, at 9 seconds, the maximum number of species are observed. As the reaction time increases beyond 9 seconds, the number of peaks begin to diminish as some of the less stable intermediates are consumed. It can be seen from the profiles that the oxidation of dodecane at these conditions results in many smaller, lower molecular weight hydrocarbon fragments. These compounds most likely consist of lower alkanes, alkenes, aldehydes, ketones, oxirans, and alcohols, which have retention times less than that of dodecane (20.5 min). Compounds with retention times above 20.5 min. are most likely C_{12} aldehydes, ketones, oxirans, and alcohols.

C. CHARACTERISTICS OF THE PREIGNITION CHEMISTRY OF DODECANE

In many ways the preignition oxidation behavior of dodecane is similar to that for lower molecular weight alkanes such as propane. The initial attack on dodecane at low temperature involves hydrogen abstraction by molecular oxygen:

$$C_{12}H_{26} + O_2 \rightarrow C_{12}H_{25} + HO_2 \qquad (97)$$

This hydrogen abstraction should almost certainly involve a secondary C-H

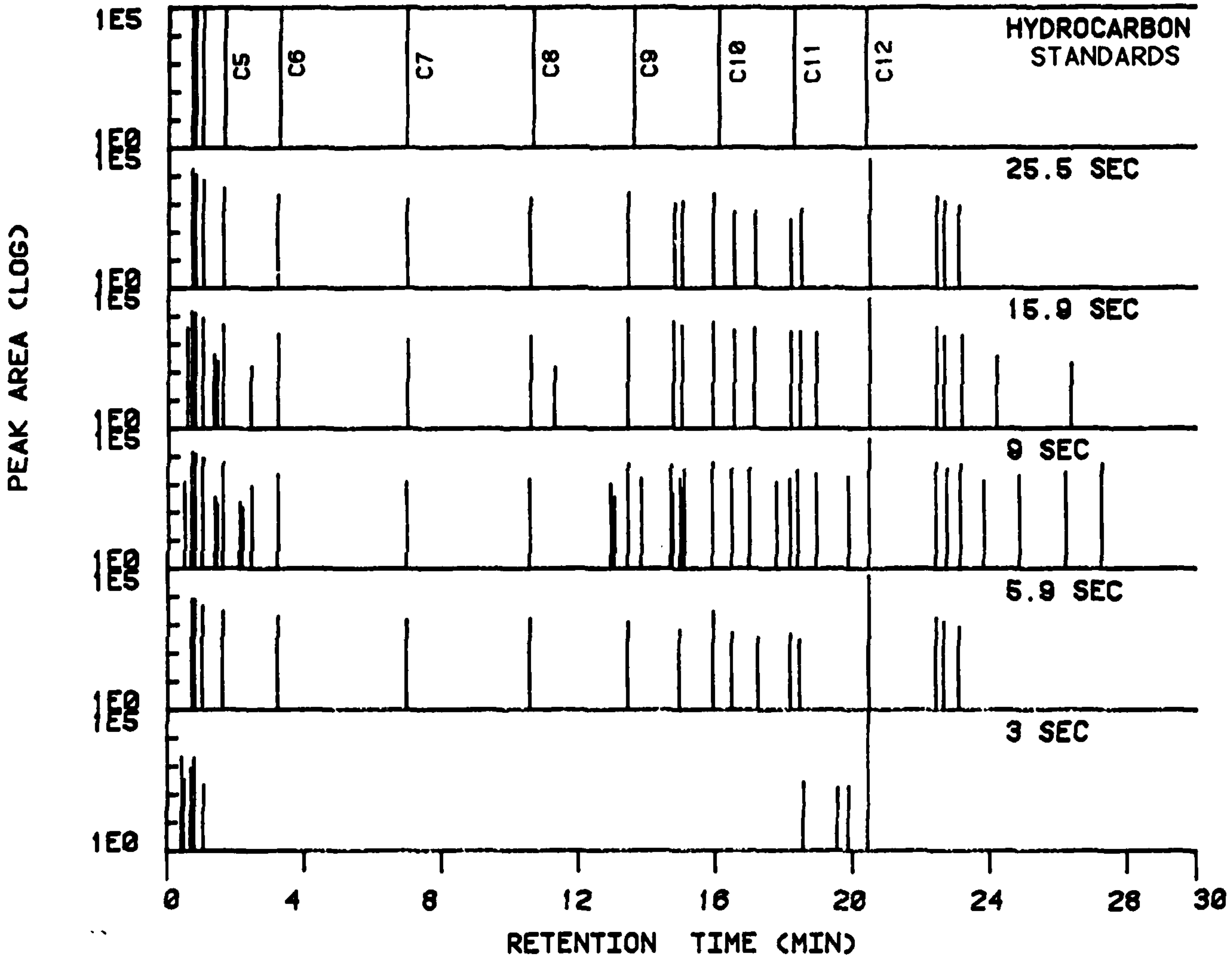

FIG. 41. CHROMATOGRAPHIC PEAK PROFILES FOR $C_{12}H_{26}$/AIR MIXTURES AT ϕ=0.9; P_o=400 TORR; T_o=523 K.

bond. Attack on a secondary C-H bond is favored energetically over that of a primary bond. In addition, with dodecane there are 20 secondary sites as compared to only 6 primary sites. Due to the abundance of secondary sites, the resulting alkyl radical (dodecyl) consists of several isomers (5) depending on the position of initial attack.

As with lower alkanes at low temperatures, oxygen addition to the alkyl radical forming an alkylperoxy radical should be favored:

$$C_{12}H_{25} + O_2 \rightarrow C_{12}H_{25}O_2 \qquad (98)$$

The major difference between the low temperature oxidation of dodecane and lower alkanes such as propane is in the manner in which the alkylperoxy radical subsequently reacts. In propane oxidation, the alkylperoxy radical tends to abstract a hydrogen, forming a hydroperoxide:

$$RO_2 + RH \rightarrow ROOH + R \qquad (10)$$

This process can also occur with dodecane; however, the dominant process with high molecular weight fuels is thought to involve the isomerization of the alkylperoxy radical by intramolecular hydrogen transfer, forming a hydroperoxyalkyl radical:

$$RO_2 \rightarrow QOOH \qquad (20)$$

The hydroperoxyalkyl radical can decompose directly, yielding a reactive OH radical and either carbonyl compounds or O-heterocycles (Fish, 1968). Alternately, a competing step is the further addition of oxygen followed by hydrogen abstraction, which yields a dihydroperoxide. Both steps can lead to a variety of oxygenated species and OH which can go on to rapidly and unselectively attack the initial fuel, accelerating the overall reaction. These two reaction paths can then explain most of the different classes of products formed from dodecane oxidation. The lower alkane product species which were observed are most likely formed by alkyl radical recombination and by hydrogen atom abstraction by alkyl radicals. The large number of different individual species formed is due to the many different alkyl radical isomers which can be initially formed.

The alkylperoxy isomerization reaction path is an accelerating route. The importance of this scheme described above, increases with increasing carbon number of the fuel. This helps to explain the higher reactivity of high carbon number fuels such as dodecane, as opposed to low carbon number fuels such as propane.

D. EXPERIMENTAL RESULTS FOR DODECANE/TETRALIN MIXTURES

1. Effect of Tetralin Addition on Ignition Limits

Tetralin was added to dodecane in concentrations of 5, 10 and 20 vol %. The pressure and temperature boundaries separating the region of slow combustion from that of cool flames and two-stage ignition are shown in Fig. 42 for combustion in air of pure dodecane and the dodecane/tetralin blends. It is apparent that at the higher temperatures the addition of up to 20% of the aromatic component has little effect on the boundary and the ignition tendency is controlled by the more ignitable component, dodecane.

At lower temperatures the tetralin begins to have a more pronounced effect on the boundary by increasing the minimum pressure at which cool flames begin to propagate at a given temperature. This effect is especially evident with the mixture containing 20% tetralin. Finally, at 523 K there is a significant increase in the minimum pressure for the occurrence of cool flames, the increase in minimum pressure being proportional to the amount of tetralin added.

These results are in agreement with those of Salooja (1968) who has shown that the ignition tendencies of binary mixtures are generally influenced by the more readily ignitable component, and this influence is greater at higher temperatures than at temperatures near the minimum ignition temperature. In addition, it was shown that for binary mixtures whose components display very

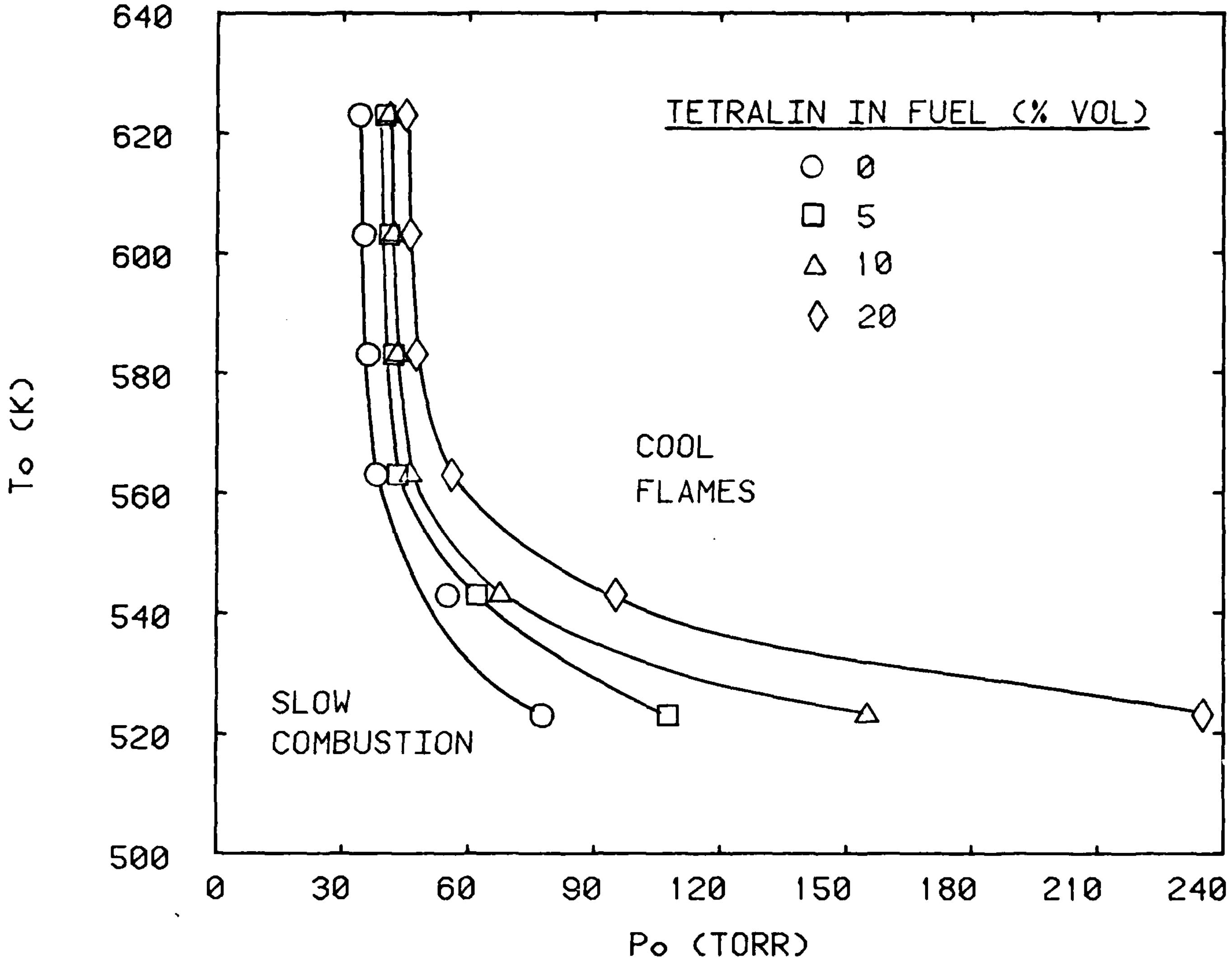

FIG. 42. PRESSURE-TEMPERATURE BOUNDARIES SEPARATING THE REGIONS OF SLOW COMBUSTION AND COOL FLAMES FOR $C_{12}H_{26}/C_{10}H_{12}$/AIR MIXTURES AT ϕ=1.0; P_o=200 TORR.

different preflame behavior, such as mixtures of straight chain alkanes with aromatics, the ignition tendencies of the mixtures vary almost linearly with the relative concentrations of the components. This was observed in the present study but only at the low end of the temperature range.

2. Effect of Tetralin Addition on Induction Period

The effect of tetralin addition on the induction period preceding the first cool flame can be seen from the plots of ln τ_{cf} against $1/T_o$ (Fig. 43). In general, for a given temperature and pressure, the induction period increases with increasing concentration of tetralin in the mixture. As in Section B, values for the apparent overall activation energy were obtained from the slopes of the fitted lines. These values are given in Table VI.

An increase in activation energy of about 25.9 kJ/mol (6 kcal/mol) is observed for the mixture with 5% tetralin over that of the pure dodecane. Further addition of tetralin up to 20% is accompanied by only a small further increase in activation energy. It has been previously shown that the activation energy is a good indicator of ignitability of pure alkanes, where E_a decreases as the ease of ignition increases (Foster, 1974).

A study of the ignition characteristics of binary mixtures of straight and branched chain alkanes (Cullis and Foster, 1974) showed that the change in ignitability of a mixture was not a result of a change in activation energy. However, the values obtained in the present study for binary mixtures of dodecane and tetralin suggest that the overall activation energy may be useful in characterizing the ignition behavior of certain mixtures.

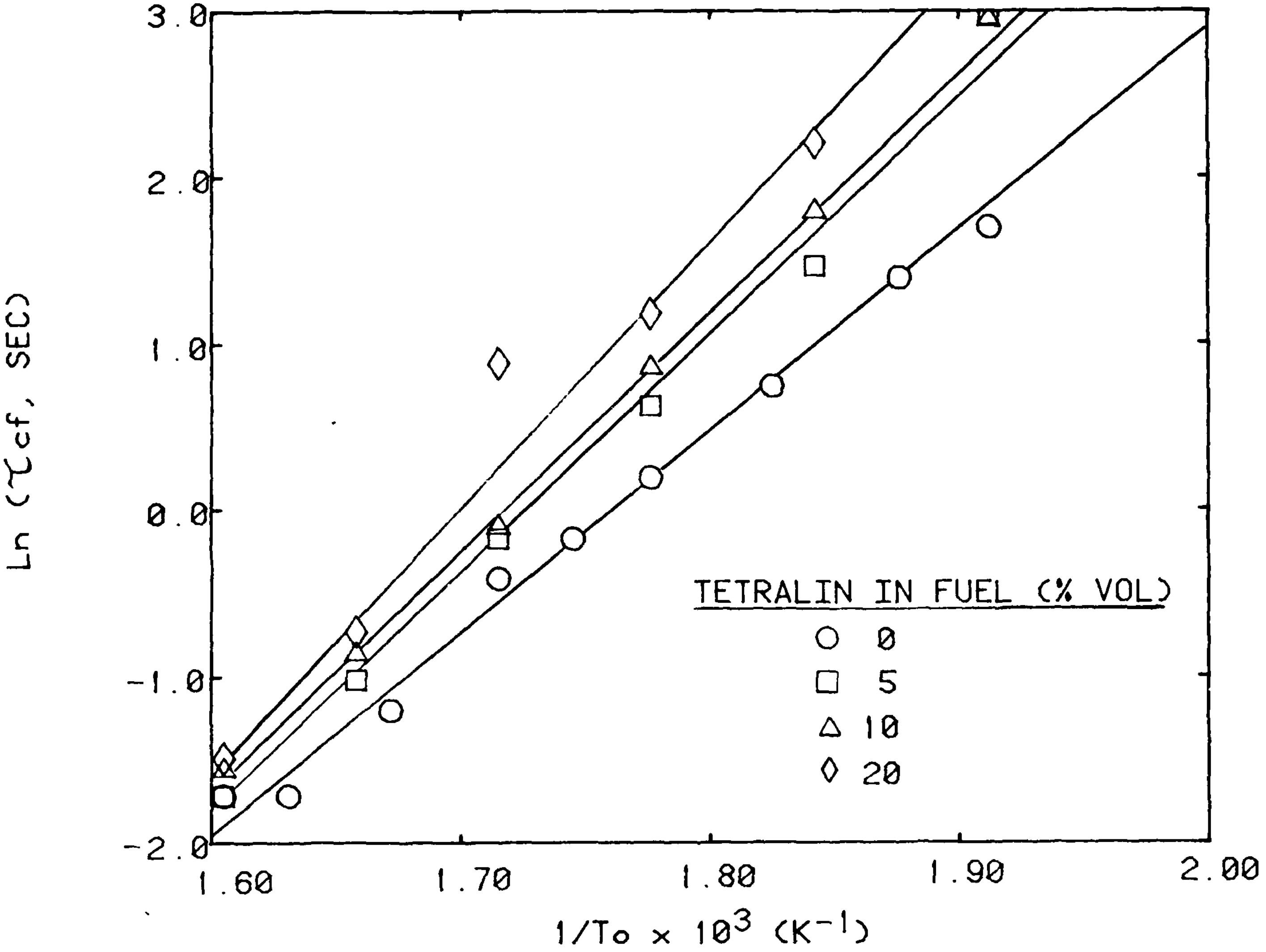

FIG. 43. EFFECT OF INITIAL TEMPERATURE ON THE INDUCTION PERIOD PRECEDING THE FIRST COOL FLAME FOR $C_{12}H_{26}/C_{10}H_{12}$/AIR MIXTURES AT Φ=1.0; Po=200 TORR.

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SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

REPORT DOCUMENTATION PAGE

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BEFORE COMPLETING FORM

1. REPORT NUMBER
16957-EG-Final Report

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (*and Subtitle*)
PREIGNITION OXIDATION CHARACTERISTICS
OF HYDROCARBON FUELS

5. TYPE OF REPORT & PERIOD COVERED
Final Report
April 15,1980-October 14,1984

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(*s*)
N.P. Cernansky, R.S. Cohen and R.D. Wilk

8. CONTRACT OR GRANT NUMBER(*s*)
DAAG29-80-C-0112

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Department of Mechanical Engineering
Drexel University
Philadelphia, PA 19104

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
U. S. Army Research Office
Post Office Box 12211
Research Triangle Park, NC 27709

12. REPORT DATE
July 1985

13. NUMBER OF PAGES
112

14. MONITORING AGENCY NAME & ADDRESS(*if different from Controlling Office*)

15. SECURITY CLASS. (*of this report*)
Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (*of this Report*)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (*of the abstract entered in Block 20, if different from Report*)

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation

19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)

Hydrocarbon Fuels, Preignition Chemistry, Oxidation, Ignition, Chemical Kinetics

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

(See reverse side)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

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SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

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propene mechanism. The experimental results for propene were and still are being used to modify and extend the mechanism of Westbrook and Pitz. The original model was developed for temperatures above 1000 K. It is now being extended to reproduce the experimental data at low and intermediate temperatures which are characteristic of the initiation of the autoignition process.

Another aspect of this research project involved the investigation of the preignition behavior of high molecular weight liquid hydrocarbons. The cool flame ignition characteristics of dodecane were examined. This included the determination of the effects of initial conditions on the induction period. The results showed that the cool flame ignition behavior of dodecane was consistent with that of lower molecular weight alkanes. However, unlike the chemistry of lower molecular weight alkanes, the main accelerating path in the oxidation of dodecane is via the alkylperoxy isomerization and decomposition route.

The effect on the ignition behavior of adding the aromatic component tetralin to dodecane was also examined. The addition of the tetralin had the overall effect of decreasing the ignitability. However, the magnitude of this effect was non-linear with respect to the amount of tetralin added.

Results from the detailed studies on propane and propene are useful for the detailed modeling of hydrocarbon oxidation. Models for these fuels can be used as submechanisms in the hierarchical approach for modeling the combustion of more complex fuels. The results of the studies on dodecane illustrate some of the similarities and differences between the oxidation of higher molecular weight fuels and that of lower molecular weight fuels. The results of the studies on the dodecane/tetralin mixtures bring attention to the complex interaction of various classes of fuel components within a mixture. It is important to examine this matter further in order to begin to understand the ignition behavior of actual multicomponent full-boiling range fuels.

VI. SUMMARY AND CONCLUSIONS

A research program to study the preignition oxidation characteristics of hydrocarbon fuels has been carried out. A static reactor test facility and gas chromatographic analysis techniques were used to assess the preignition oxidation chemistry by determining the stable reaction intermediates and products formed during the preignition process. Experimental results for single-component, low molecular weight gaseous fuels, single-component, high molecular weight liquid fuels, and binary mixtures of liquid fuels were used to identify the important fuel (chemical) and physical factors influencing ignition behavior.

A comprehensive study was made of the oxidation of propane at low and intermediate temperatures (550-750 K). Results showed a clear transition in the oxidation chemistry, going from a low temperature regime (<600 K) to an intermediate temperature regime (650-1000 K), separated by a region of negative temperature coefficient (600-650 K). The lower temperature regime is dominated by alkylperoxy radicals and the hydrocarbon reaction products consist mainly of oxygenated species such as aldehydes, oxirans, and alcohols. In the intermediate temperature regime, hydroperoxyl radicals become dominant and the hydrocarbon products consist mainly of lower alkanes and alkenes. The effect of increasing the surface-to-volume ratio of the reaction vessel was to enhance the heterogeneous termination, resulting in longer reaction times. However, it was demonstrated that the amount of surface did not alter the main reaction paths of the mechanism.

The low and intermediate temperature preignition oxidation of propene was also studied. It was found that because of the resonance stability of the allyl radicals, reactions involving the addition of molecular oxygen to the allyl radical and the addition of radicals such as HO_2 and OH to the fuel are important, and form the basis of the low and intermediate temperature

In mixtures where both aromatics and aliphatics are present, such as with tetralin and dodecane, there is a competition between the different compounds for oxygen and radicals. As the resulting aromatic compounds are stable, they will tend to inhibit the rapid propagation of the reaction. Thus, the overall reaction will be slowed. From the experimental results, it is apparent that only a small amount of aromatic is needed to accomplish this, as only 5% added tetralin reduced the ignition tendency by over 25%.

Preliminary results of a study on the ignition behavior of ternary mixtures of dodecane, tetralin, and iso-octane confirm the complex effect of mixtures on ignitability. The ignitability of an 80% dodecane/10% tetralin/10% iso-octane mixture was less than that of either an 80% dodecane/20% tetralin mixture or an 80% dodecane/20% iso-octane mixture. Thus, the interaction of the three different fuel components produces a non-linear synergistic effect on the ignition tendency of the mixture. These effects must be determined in order to understand the detailed ignition behavior of full-boiling range fuels.

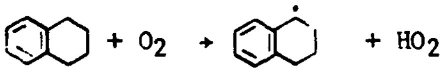
TABLE VI. Overall Activation Energies for Dodecane/Tetralin Mixtures

% Tetralin in Mixture	Ea (kJ/mol)
0	97.1
5	123.0
10	124.7
20	130.1

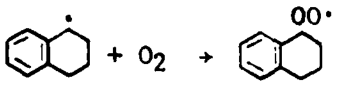
3. Characteristics of the Chemical Effects of Tetralin at Low Temperatures

In the previous section, it was shown that the addition of the tetralin had an inhibiting effect on the ignition tendency of dodecane. This effect, though, was non-linear. A small amount of the added aromatic component produced a substantial increase in the overall activation energy while further addition produced only a small further increase in E_a. In order to begin to understand this complex ignition behavior of fuel mixtures, it is necessary to examine the interaction of the oxidation chemistry of each of these components.

Aromatic hydrocarbons are, in general, difficult to ignite. At low temperatures, the initial reaction path is similar to that of aliphatic fuels. This involves hydrogen abstraction from the initial fuel followed by oxygen addition to form a peroxide compound (Santoro and Glassman, 1979). For tetralin, these steps would be:



(99)



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The resulting radicals from the aromatic fuels are relatively stable as compared to alkyl radicals, which are much more reactive. Thus aromatic compounds will tend to undergo oxidative degradation much less readily

Item 20

ABSTRACT

A research program to study the preignition oxidation characteristics of hydrocarbon fuels has been carried out. A static reactor test facility and gas chromatographic analysis techniques were used to assess the preignition oxidation chemistry by determining the stable reaction intermediates and products formed during the preignition process. Comprehensive studies were made of the oxidation of propane and propene at low and intermediate temperatures (550-750 K) and at subatmospheric pressures. The experimental results for each of these fuels demonstrated a clear transition in the oxidation chemistry from a low temperature regime to an intermediate temperature regime, separated by a region of negative temperature coefficient. The main characteristics and features of the oxidation mechanisms were determined for each fuel in each temperature regime. Increasing the vessel surface-to-volume ratio had the effect of enhancing heterogeneous termination, but did not affect the main reaction paths of the mechanism. The experimental results for propene were used to modify and extend the high temperature mechanism of Westbrook and Pitz to low and intermediate temperatures. Studies were also made of the preignition behavior of dodecane and binary mixtures of dodecane and the aromatic component tetralin. Addition of the tetralin to dodecane had the overall effect of decreasing the ignition tendency, although the magnitude of this effect was not proportional to the amount added.