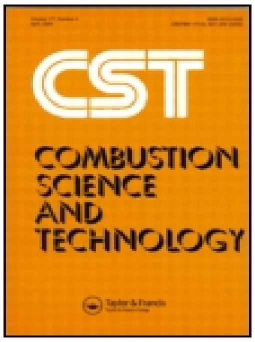

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The Oxidation of Propane at Low and Transition Temperatures

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Abstract—An experimental study of the oxidation of propane in the temperature range 563–743 K was carried out using a static reactor. The oxidation mechanism was found to undergo a transition from a low temperature reaction regime ($T < 600$ K) to that of an intermediate temperature regime ($T > 650$ K) separated by a region of negative temperature coefficient (600–650 K). In the lower temperature regime alkylperoxy 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. At the intermediate temperatures hydroperoxyl radicals are dominant and lead to hydrogen peroxide, which is the main branching intermediate in this regime. 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. The negative temperature coefficient and the change in mechanism are due to the competition between reactions involving the addition of O_2 to the alkyl radical forming the alkylperoxy radical and reactions involving the abstraction of hydrogen from the alkyl radical by O_2 to form the conjugate alkene and the hydroperoxyl radical. The effect of increasing the reaction 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. Some aspects of the mechanism at these temperatures are compared to those in the high temperature regime ($T > 1000$ K).

INTRODUCTION

The study of the chemical processes in combustion are important as they lead to the development of chemical kinetic reaction mechanisms which can be used to model various combustion systems. When considering hydrocarbon oxidation, it should be realized that reaction mechanisms are dependent on the physical conditions of the combustion environment. A change in the conditions can lead to changes in the relative importance of individual reactions which comprise the mechanism. Reaction mechanisms are especially dependent on temperature. Although actual combustion devices operate mainly at high temperatures (>1000 K), there are generally large temperature gradients in these devices during system operation. The fuel passes through and can spend considerable time at lower temperatures (600–1000 K). For example, the autoignition process in CI engines as well as end-gas autoignition and knock in SI engines are initiated at these lower temperatures. Consequently, the oxidation chemistry in this temperature range can have an important role in the overall combustion process.

The oxidation of 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 low temperature hydrocarbon oxidation is the negative temperature coefficient of reaction rate. For many hydrocarbons there exists a temperature range (50–100 degrees), usually falling between about 573 and 673 K, in which the reaction rate decreases with increasing temperature. Many believe this to be a transition region separating a low temperature and an intermediate temperature reaction regime, where the importance of the lower temperature mechanism diminishes before the intermediate temperature mechanism becomes important.

Low temperature hydrocarbon oxidation has been the subject of extensive study in the past. Most of this 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 considerable attention is propane (Pease *et al.*, 1934, 1938; Newitt and Thornes, 1937; Knox and Norrish, 1954; Lefebvre and Luquin, 1965; Gray and Felton, 1974; Shtern and coworkers, 1969, 1974, 1976, 1984). Propane is the simplest fuel which exhibits cool flame and negative temperature coefficient characteristics and yet it has properties which are generally representative of those of higher molecular weight alkane hydrocarbons. This paper presents results of an additional experimental study of propane oxidation, providing new data on the mechanism at low and intermediate temperatures.

The experimental system employed for this work consists of a static reactor and incorporates gas chromatographic analysis for determining the stable reaction intermediates and products. One of the main objectives for this particular study was to supplement the existing knowledge of the low temperature oxidation behavior of propane. Much of the earlier work was done in the 1930s–1950s, before the development of 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. Another 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 this study, the effects of initial temperature, initial pressure, equivalence ratio, and vessel surface-to-volume ratio on the oxidation behavior were examined. In addition, different temperature regimes of reaction dominance were identified, including the region of negative temperature coefficient (NTC). The main reaction paths and characteristics of the oxidation mechanism in these temperature regimes were determined.

EXPERIMENTAL FACILITY AND PROCEDURES

The experimental facility, shown in Figure 1, is similar to that used in previous work by Wilk *et al.* (1982) and 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

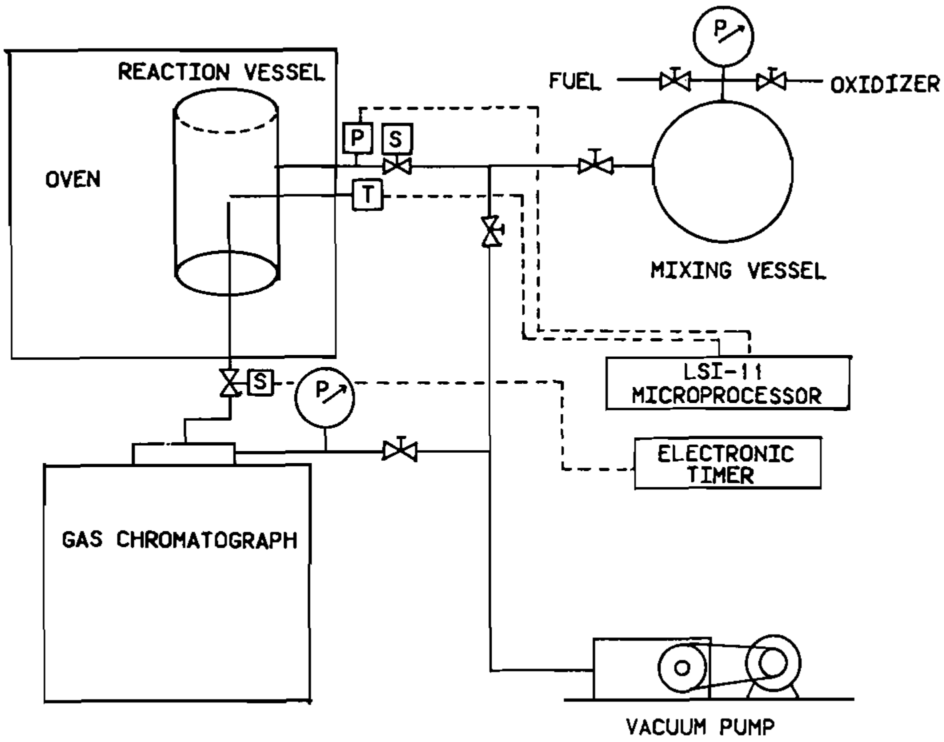

FIGURE 1 Experimental facility.

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 Pt/Pt–13% Rh thermocouple constructed of 0.05 mm diameter wires, which were passed through a 1.58 mm diameter alumina insulator. To protect against catalytic heating caused by the platinum wire, the thermocouple was coated with a thin layer of silica.

A spherical Pyrex mixing vessel (volume 2125 cm^3) was used to mix the reactants. The desired mixture ratio of 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 min. Following the mixing process, the gaseous mixture was rapidly admitted into the evacuated, preheated reaction vessel by way of a solenoid valve, at which point the reactions commenced. The pressure and temperature of the reaction vessel were measured and followed in time as the reactions progressed, and, at a selected time during the reaction, the experiment was terminated by withdrawing a portion (20 percent) 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 s to obtain a sample of adequate size for chromatographic analysis. This sampling yielded excellent temporal resolution considering the slowness of reaction under the present conditions, taking on the order of hundreds of seconds.

A gas sampling valve was used to inject a portion of the acquired samples (0.25 cm) into a Varian 3700 gas chromatograph equipped with a flame ionization detector (FID). The sample was carried by helium carrier gas and separated on a 2.4 m long × 0.3175 cm diameter Porapak Q 80/100 mesh packed column. A nickel catalyst, located downstream of the column was used to methanize the carbon oxides, facilitating their detection on FID. Temperature programming (5 min at 30°C; 8°C/min to 160°C) was used to obtain adequate separation of the carbon oxides and most of the stable hydrocarbons present in the sample. The uncertainty in the species measurements was ± 3 percent for the alkanes, alkenes and carbon oxides, and ± 6 percent for the oxygenated hydrocarbons. Other species expected to be present but not monitored were: H_2, O_2, H_2O, and H_2O_2. Formaldehyde formation was expected to be monitored; however, 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 peak 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 (20–30) runs were required to condition (age) the surface before the data became reproducible. The criteria for reproducibility was that the induction period not vary more than 2 percent, 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–time traces were carefully monitored up to the point of sample withdrawal.

High purity propane (99.5 percent) and air (99.99 percent) were used for this work. Experiments were carried out at initial temperatures ranging from 563 to 743 K, initial pressures from 440 to 657 torr, and equivalence ratios from 0.8 to 4.0. In order to examine the effects of vessel surface area, a second reaction vessel was fitted with a concentric Pyrex insert. The volume was kept constant by slightly increasing the length of the vessel to compensate for the volume taken up by the insert. The surface-to-volume ratio of the second reaction vessel was then $1.2\ \text{cm}^{-1}$, as compared to $0.5\ \text{cm}^{-1}$ for the primary vessel.

EXPERIMENTAL RESULTS AND DISCUSSION

Cool Flames and Negative Temperature Coefficient

The experimental results confirm the autocatalytic nature of the low temperature oxidation of propane. It can be seen in Figures 2 and 3 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

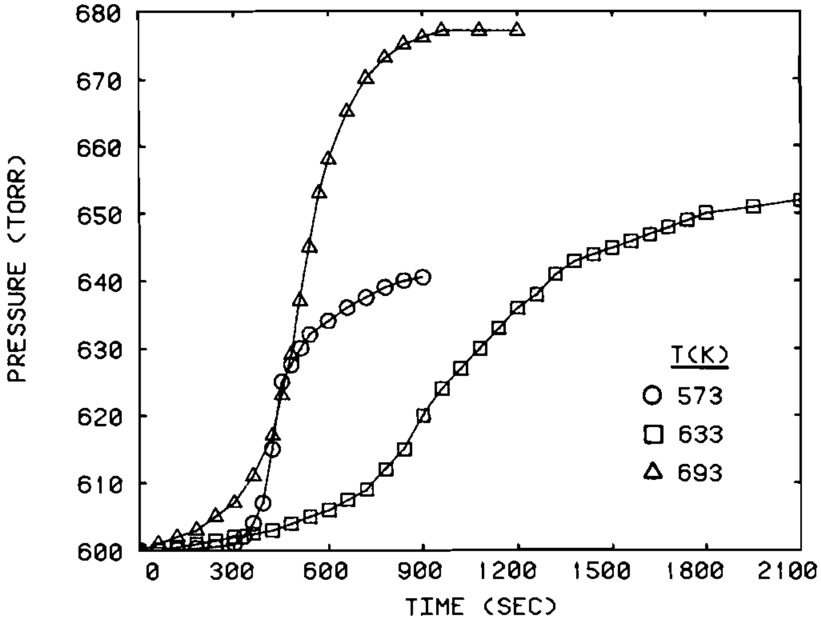

FIGURE 2 Effect of initial temperature on the pressure histories for C_3H_8/air mixtures at $\phi=2.0$.

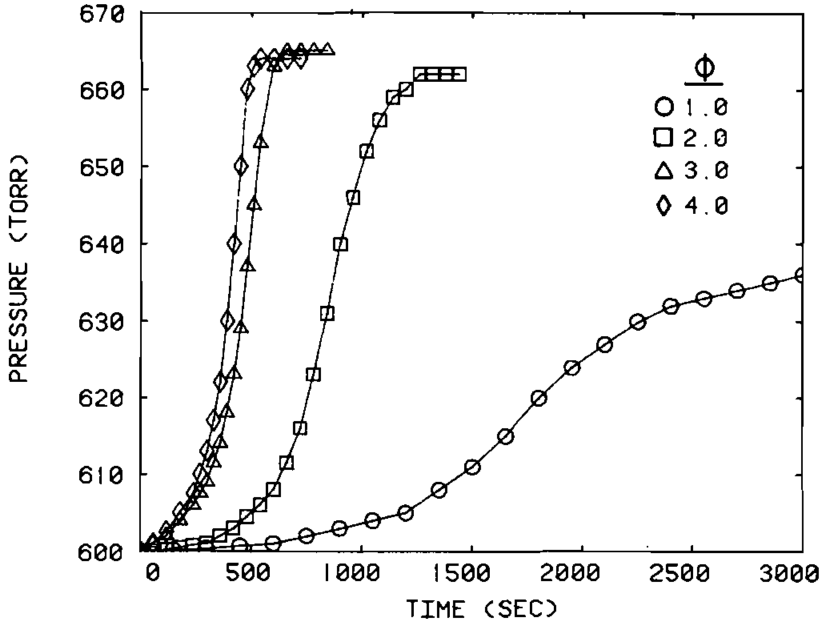

FIGURE 3 Effect of equivalence ratio on the pressure histories for C_3H_8/air mixtures at $T_0=673$ K.

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 (Figures 4 and 5) 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 nonadiabatic, 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 therefore, is 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 rate begins to slow again.

The initial temperature has an interesting effect on the induction period (Figure 6) and on the maximum rate of pressure rise (Figure 7). 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 to 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), Gray and Felton (1974) (623–673 K), and Levitsky *et al.* (1984) (613–658 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 (Figure 8), as well as by thermal pulses on the temperature profiles (Figure 9). These pulses were predominantly for fuel-rich mixtures ($\phi > 1.0$), and at the richest conditions examined ($\phi = 3.0$, 4.0) multiple oscillations were observed. Increasing the propane concentration in the mixture increased both the number and intensity of the cool flames (Figure 10). The occurrence of the cool flames produced pressure rises up to 60 torr and temperature rises up to 40 degrees.

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

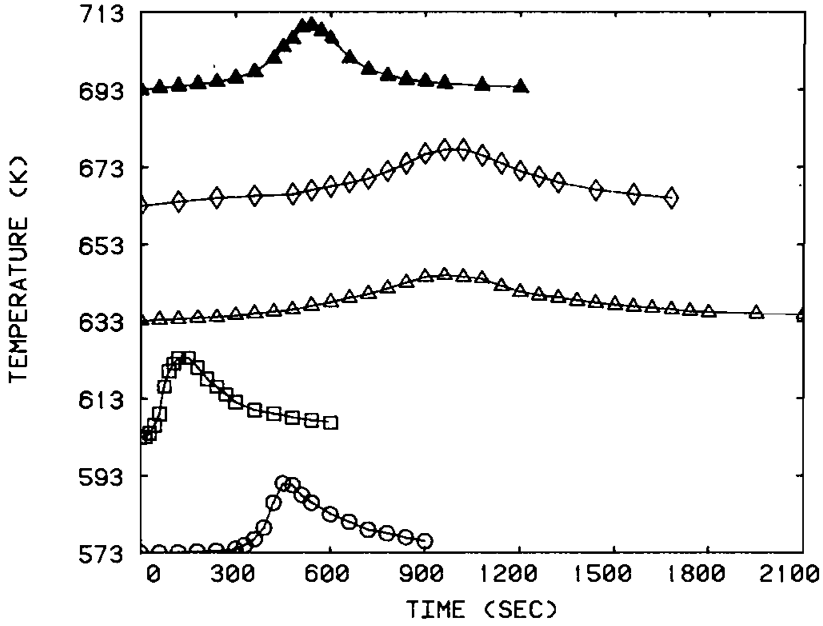

FIGURE 4 Effect of initial temperature on the temperature histories for C_3H_8/air mixtures at $\phi = 2.0$; $P_0 = 600$ torr.

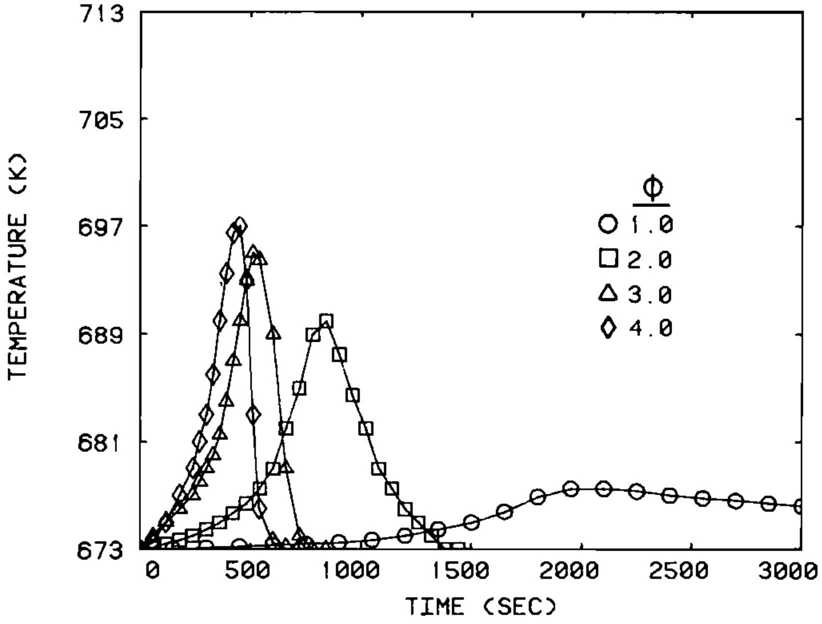

FIGURE 5 Effect of equivalence ratio on the temperature histories for C_3H_8/air mixtures at $P_0 = 600$ torr.

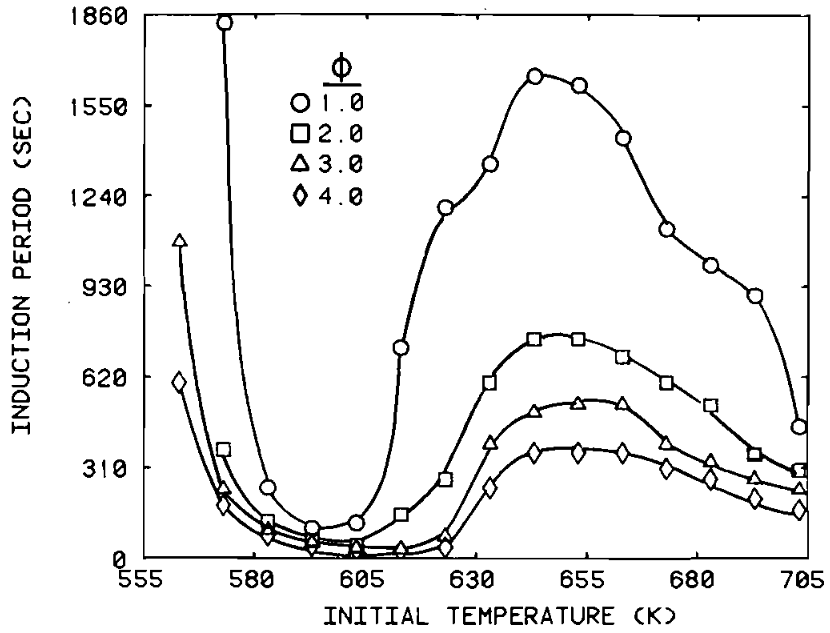

FIGURE 6 Effect of initial temperature and equivalence ratio on the induction period. $P_0=600$ torr.

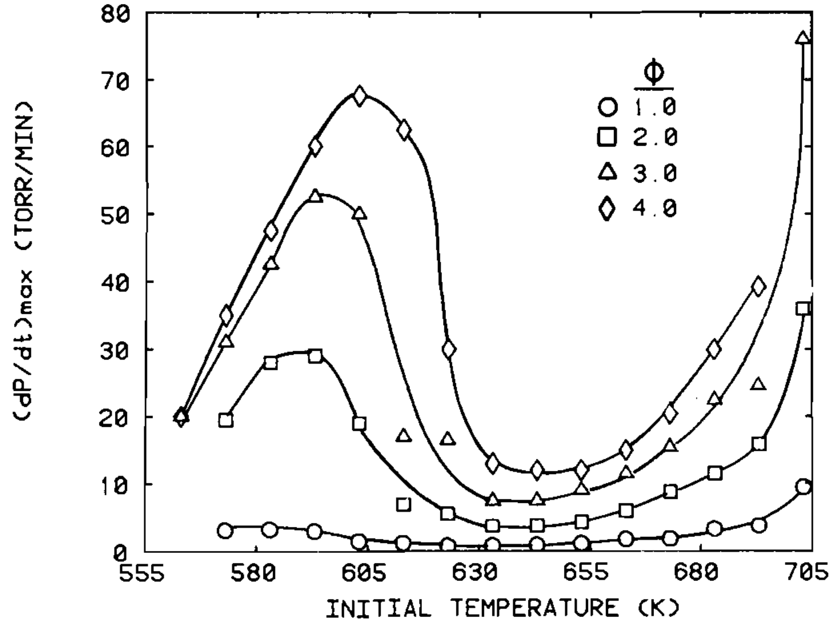

FIGURE 7 Effect of initial temperature and equivalence ratio on the maximum rate of pressure rise.

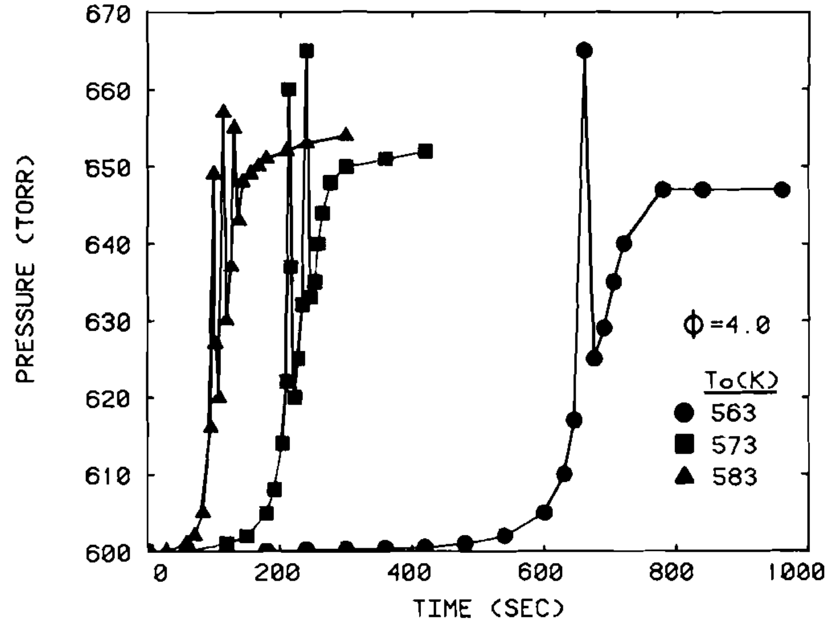

FIGURE 8 Effect of initial temperature on the pressure histories and cool flames for C_3H_8/air mixtures.

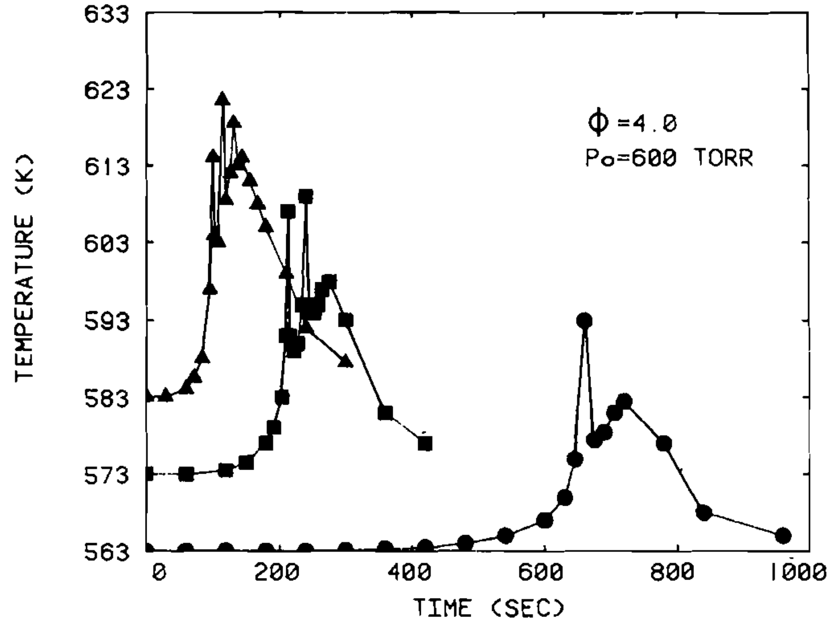

FIGURE 9 Effect of initial temperature on the temperature histories and cool flames for C_3H_8/air mixtures.

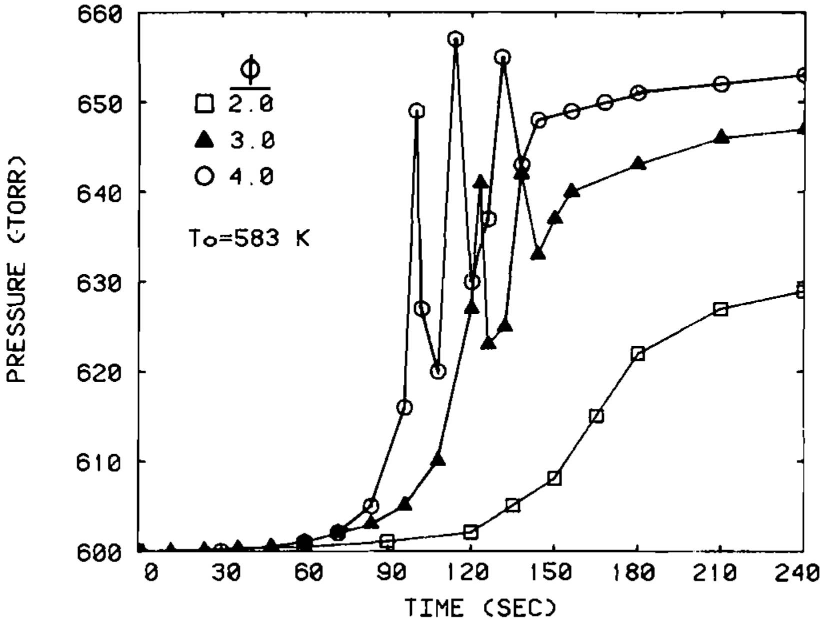

FIGURE 10 Effect of the equivalence ratio on the pressure histories and cool flames for C_3H_8/air mixtures.

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:

$$\tau_{mr} = A \exp(E_a/RT_0),$$

where, in this case, the characteristic time used (τ_{mr}) was that employed by Nguyen *et al.* (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 pre-exponential constant and T_0 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 *et al.* (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 percent which is 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 characteristic reaction time (τ_{mr}) from which these overall activation energies were determined may not be strictly a chemical time. From Figures 2–5, the maximum rate of pressure rise corresponds to the time at which the maximum temperature occurs (where the rate of heat loss is maximum). Therefore, it seems that τ_{mr} depends on both physical and chemical phenomenon.

A more appropriate characteristic time to use for determining overall activation energies is the induction period (τ). Since τ is the time until the beginning of the pressure rise, it is less dependent on the physical phenomenon, as the heat loss from the vessel in this stage of the reaction is very small. Thus τ depends more on the overall chemical reaction rate. Overall activation energies determined from induction period data should then be a better measure of the preflame chemistry. The induction period data yielded a low temperature activation energy of 55 kcal/mol and an intermediate temperature activation energy of 23 kcal/mol.

The effect of varying the initial pressure on the reaction can be seen by examining Figure 11, 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 s 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.

Species Measurements

Results from the analytical species measurements are shown in Figures 12 and 13, 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 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 per-

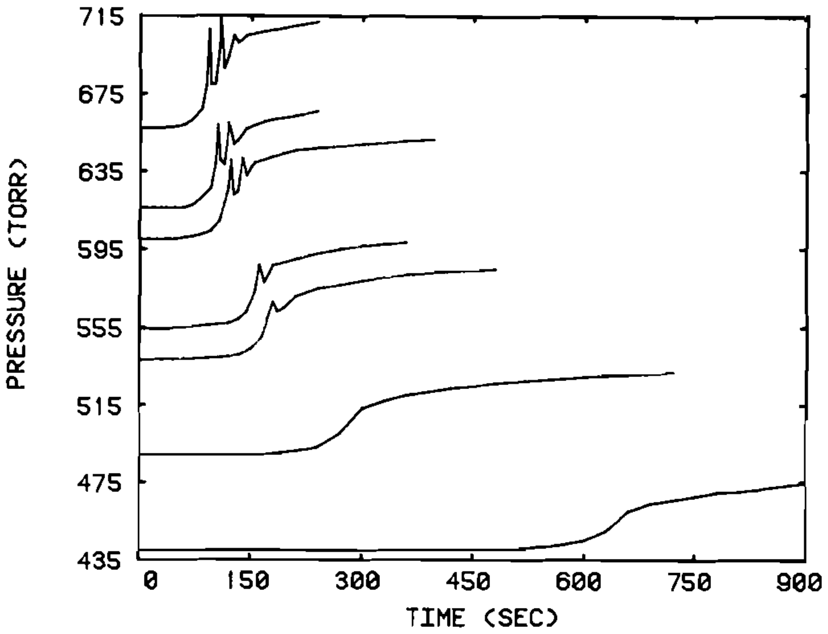

FIGURE 11 Effect of initial pressure on the pressure histories for C_3H_8/air mixtures at $\phi=3.0$, $T_0=583$ K.

cent of the total combined quantity for the case at 583 K and about 88 percent 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 percent. At 683 K, these same minor products were measured, each with a maximum concentration less than 0.16 percent. 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 percent.

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 (Figure 12) to 683 K in the intermediate temperature regime (Figure 13). The amount of propane consumed increases with temperature from about 59 percent at 583 K to about 80 percent 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 percent and that of methanol decreases by about 82 percent as the temperature is increased from 583 K to 683 K. On the other hand, the maxi-

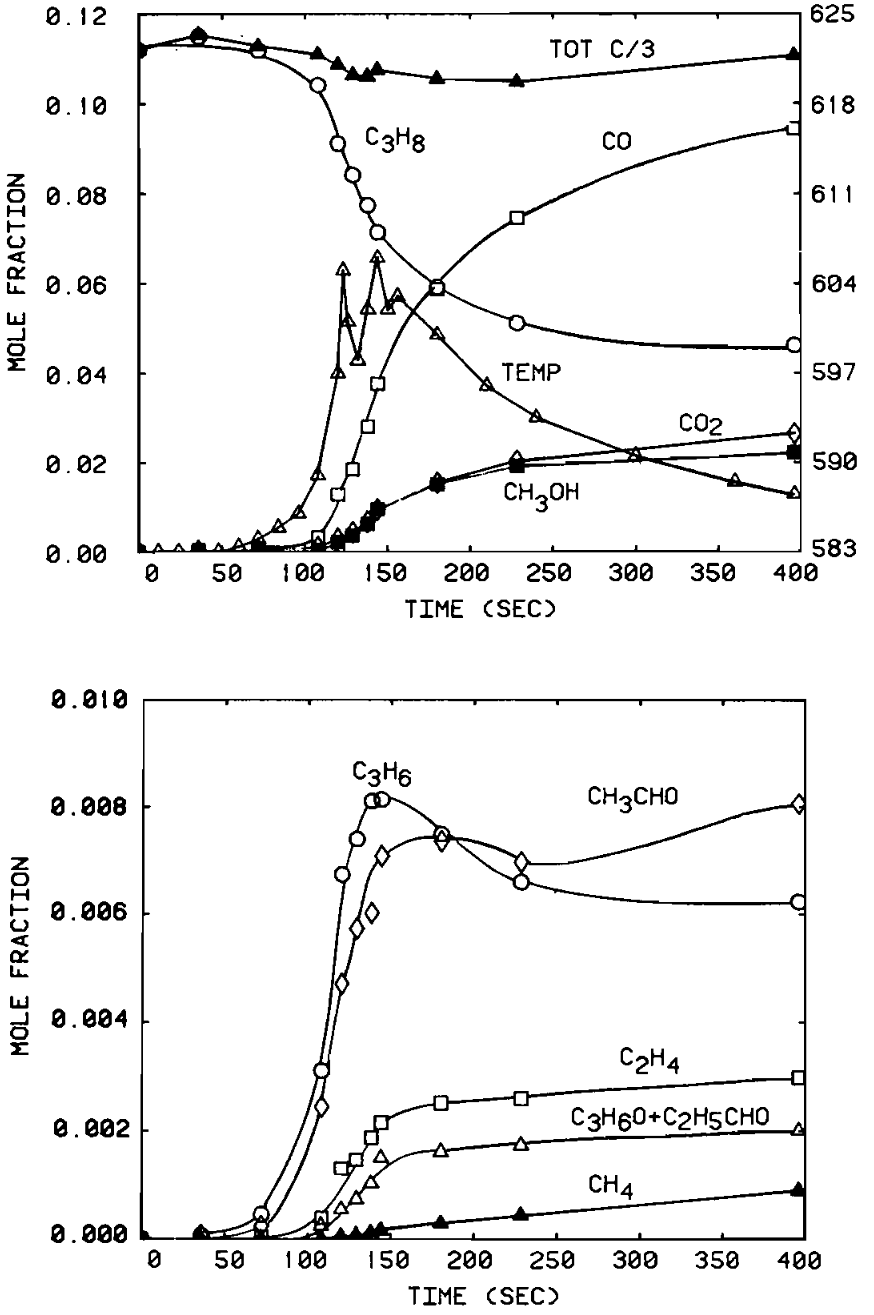

FIGURE 12 Species concentration and temperature profiles for C_3H_8/air mixtures at $\phi=3.0$; $P_0=600$ torr; $T_0=583$ K.

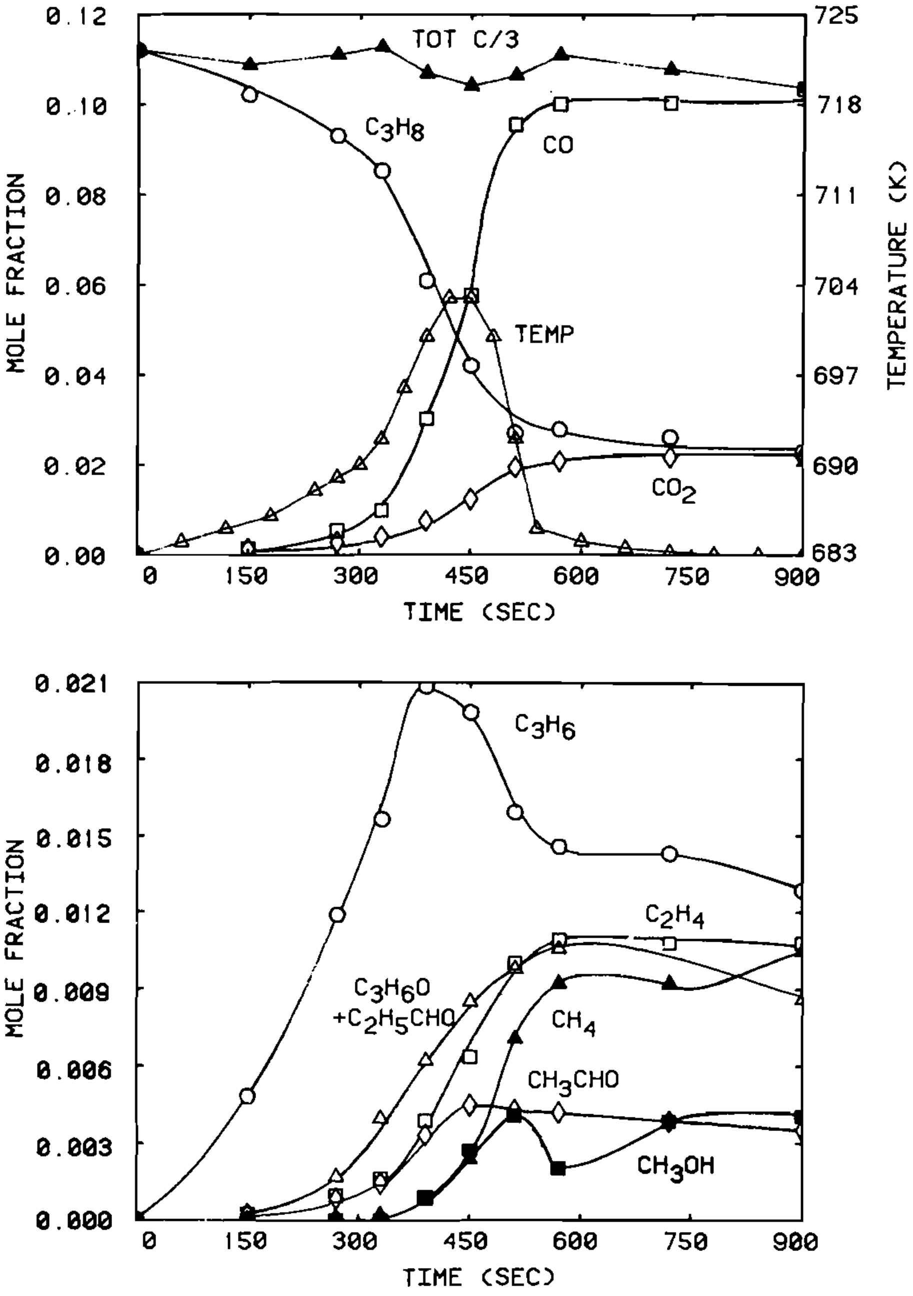

FIGURE 13 Species concentration and temperature profiles for C_3H_8/air mixtures at $\phi=3.0$; $P_0=600$ torr; $T_0=683$ K.

mum net yield of propene increases by 157 percent, that of ethene by 275 percent and that of methane by a dramatic 1200 percent. An exception to this trend is with propene oxide, the concentration of which increases by about 400 percent 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 Figure 12. 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 Figures 14–17. It can be seen from Figures 14 and 15 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, $\phi=1.0$ (Figure 16), 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 $\phi=0.8$ (Figure 17), the reaction did not accelerate to hot ignition but behaved as the other intermediate temperature cases.

Surface Effects

The effect of increased vessel surface-to-volume ratio was examined. An experiment was performed in the higher S/V reaction vessel under the same conditions as in Figure 13. The species concentration and pressure and temperature profiles obtained for the higher S/V vessel are presented in Figures 18, 19, and 20 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 temperature rises. 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 temperature rise 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 a 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 (Figure 21). 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), Aleksishvili *et al.* (1974), and Baldwin *et al.* (1977).

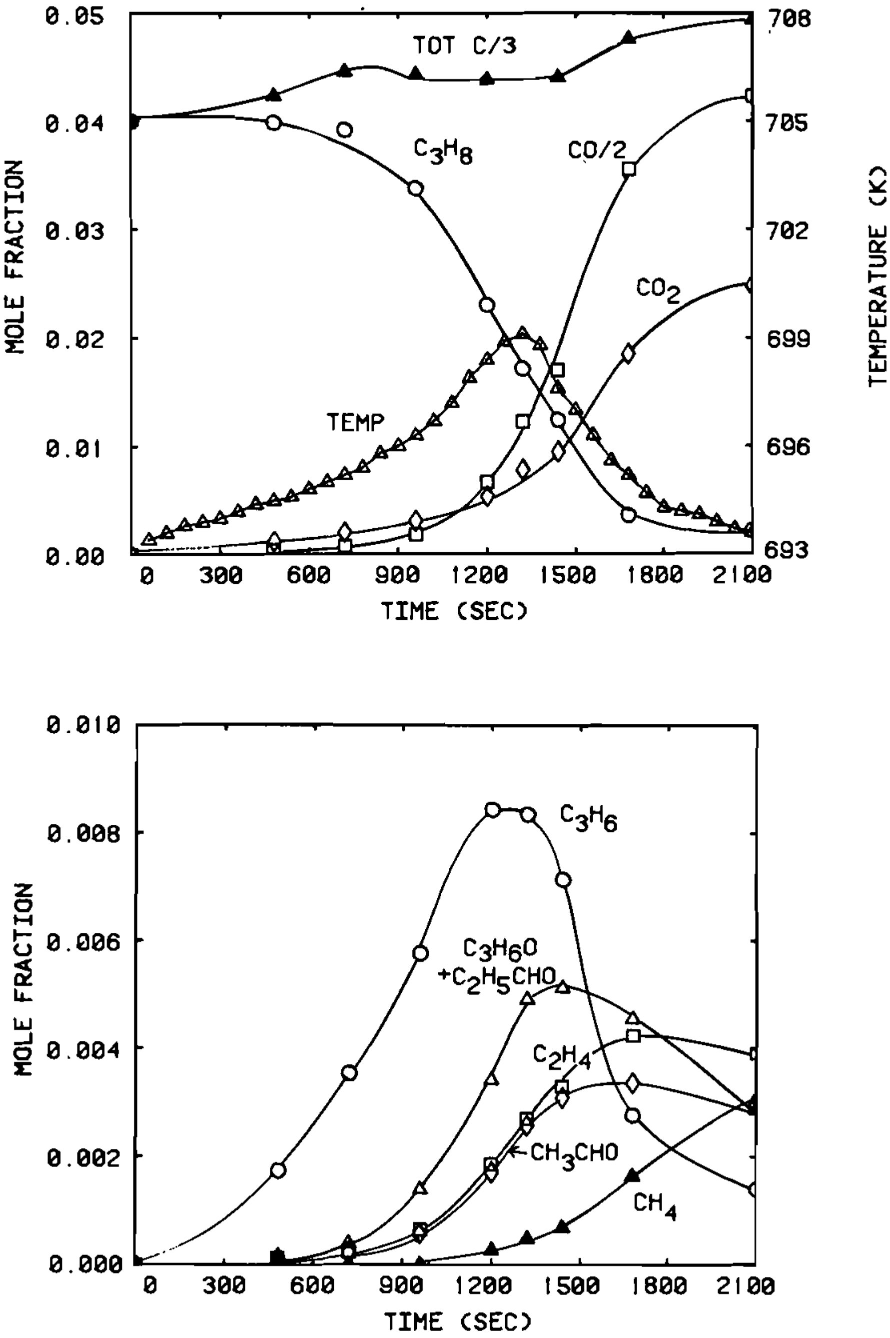

FIGURE 14 Species concentration and temperature profiles for C_3H_8/air mixtures at $\phi = 1.0$; $P_0 = 600$ torr; $T_0 = 693$ K.

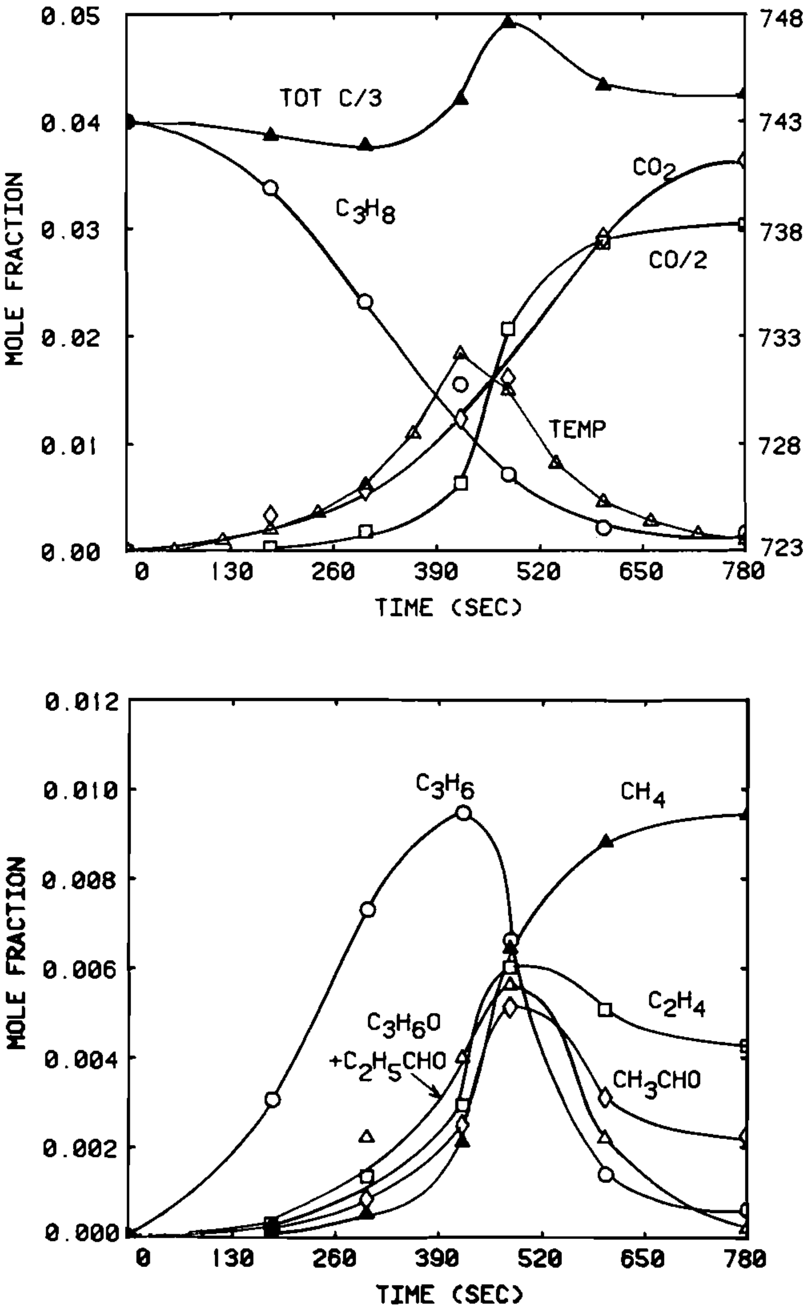

FIGURE 15 Species concentration and temperature profiles for C_3H_8/air mixtures at $\phi = 1.0$; $P_0 = 600$ torr; $T_0 = 723$ K.

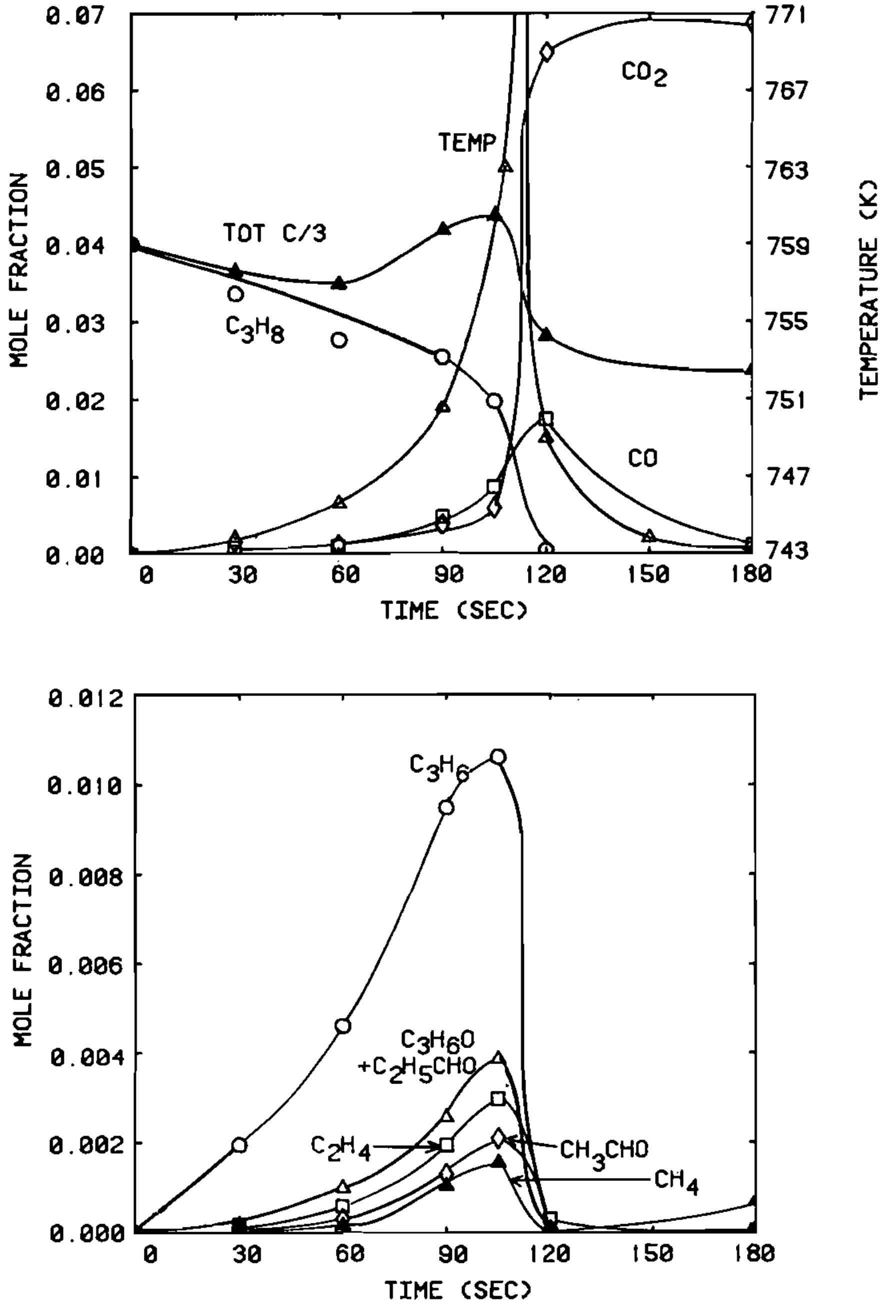

FIGURE 16 Species concentration and temperature profiles for C_3H_8/air mixtures at $\phi=1.0$; $P_0=600$ torr; $T_0=743$ K.

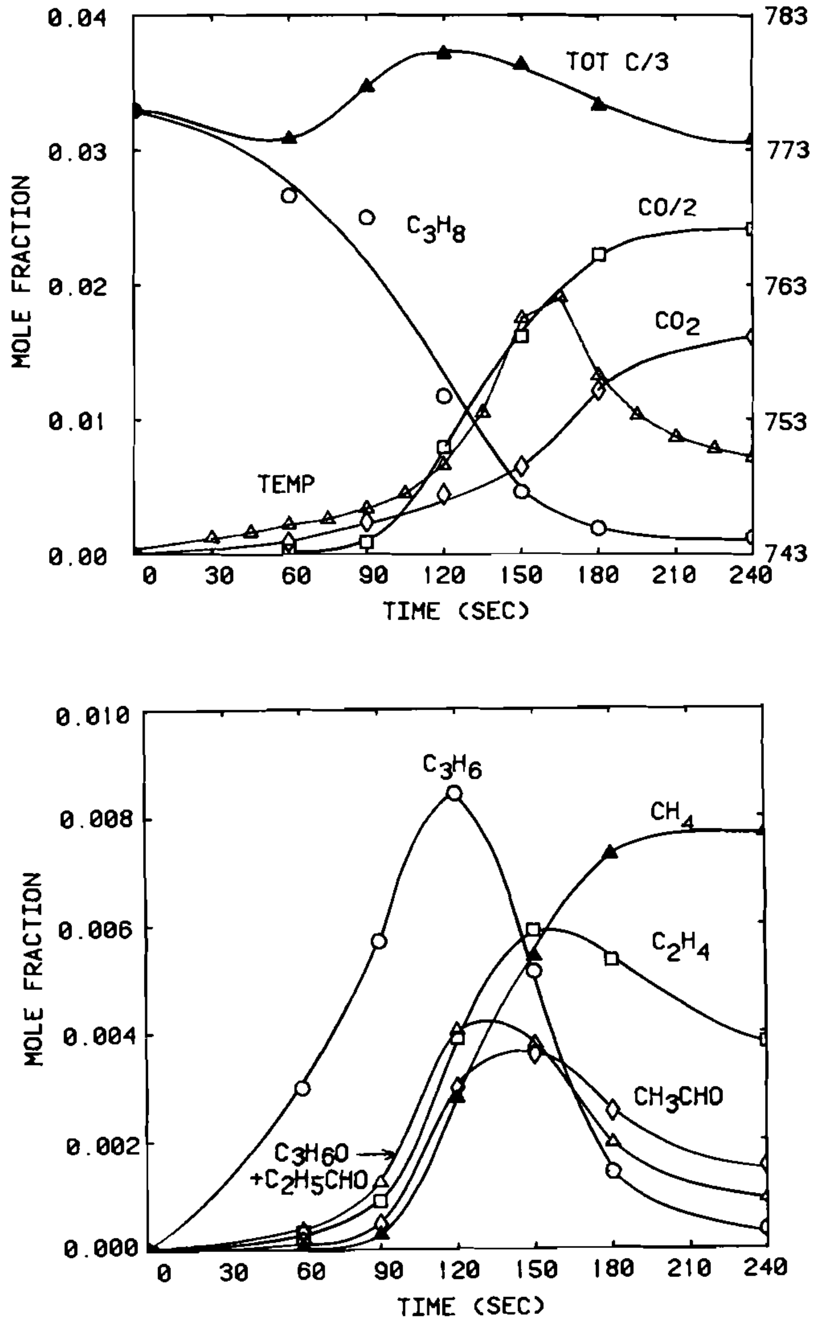

FIGURE 17 Species concentration and temperature profiles for C_3H_8/air mixtures at $\phi=0.8$; $P_0=600$ torr; $T_0=743$ K.

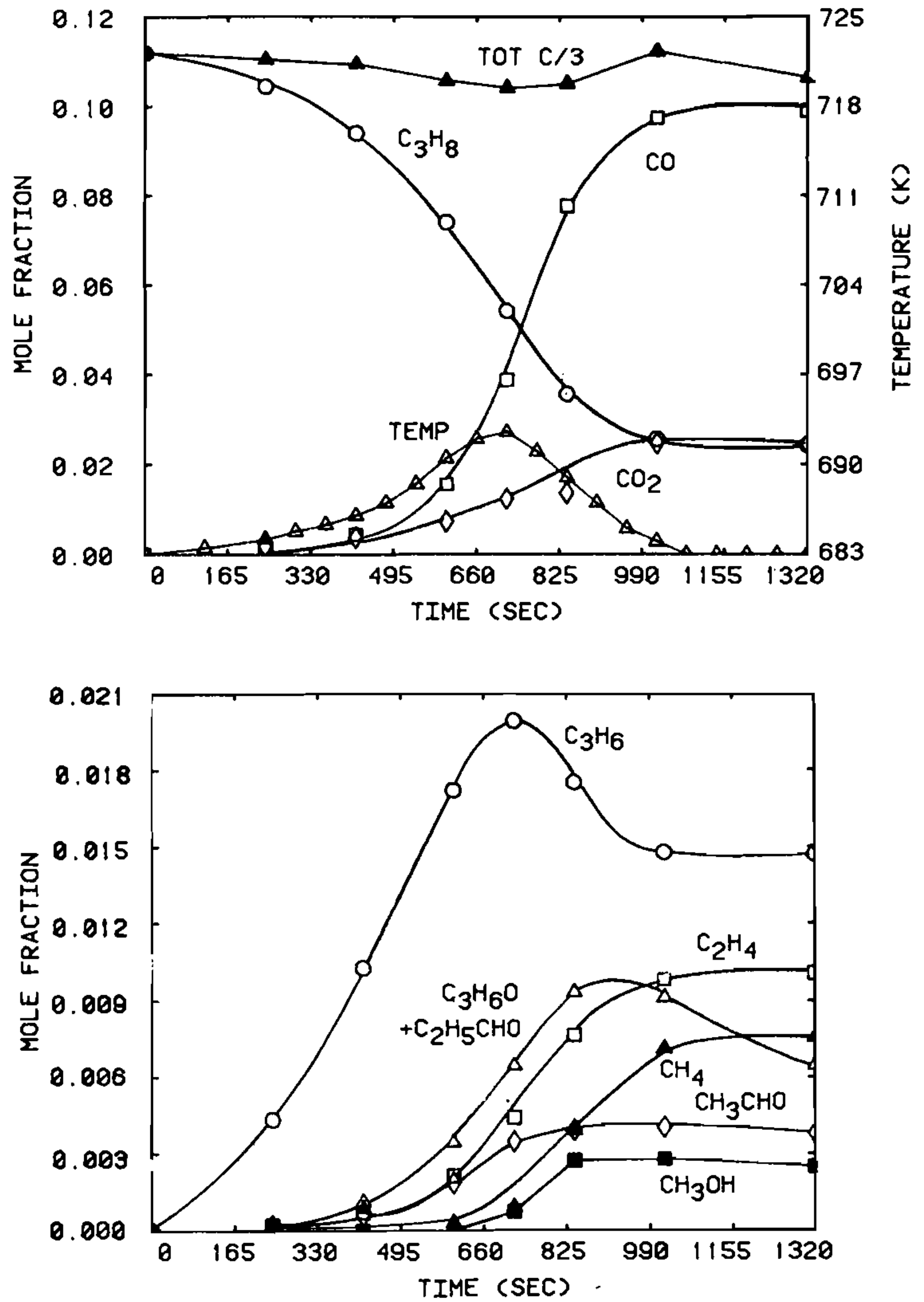

FIGURE 18 Species concentration and temperature profiles for C_3H_8/air mixtures at $\phi = 3.0$; $P_0 = 600$ torr; $T_0 = 683$ K. Surface-to-volume ratio $= 1.2\ \text{cm}^{-1}$.

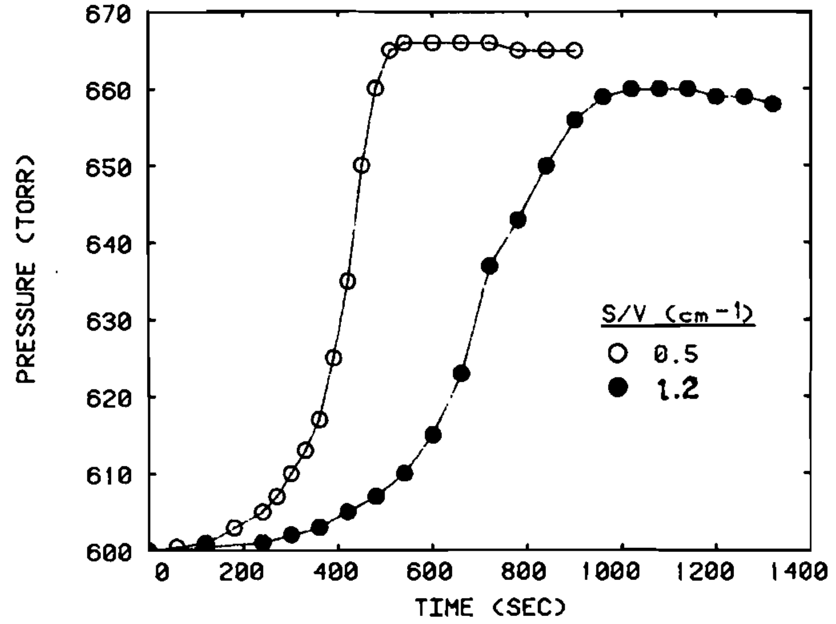

FIGURE 19 Effect of surface-to-volume ratio on the pressure histories for C_3H_8/air mixtures at $\phi=3.0$; $T_0=683$ K.

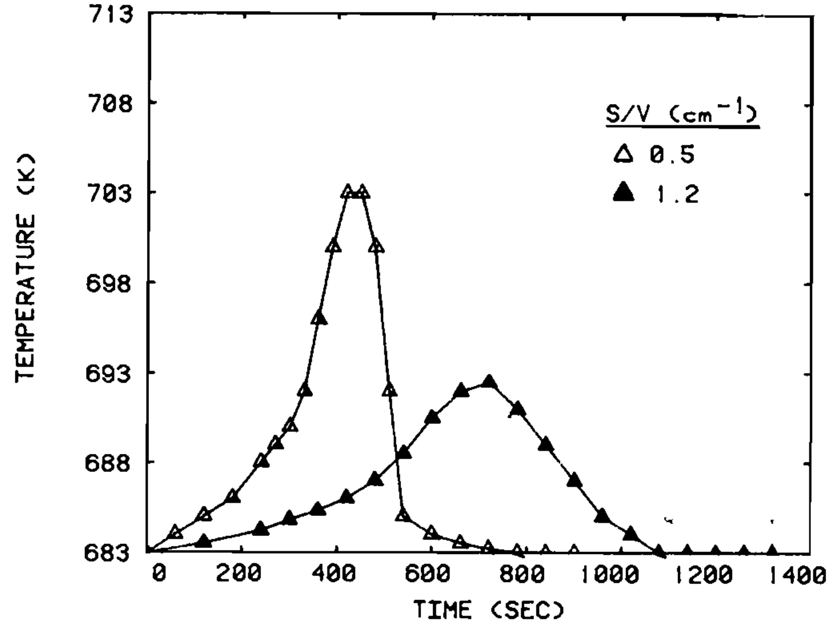

FIGURE 20 Effect of surface-to-volume ratio on the temperature histories for C_3H_8/air mixtures at $\phi=3.0$; $P_0=600$ torr.

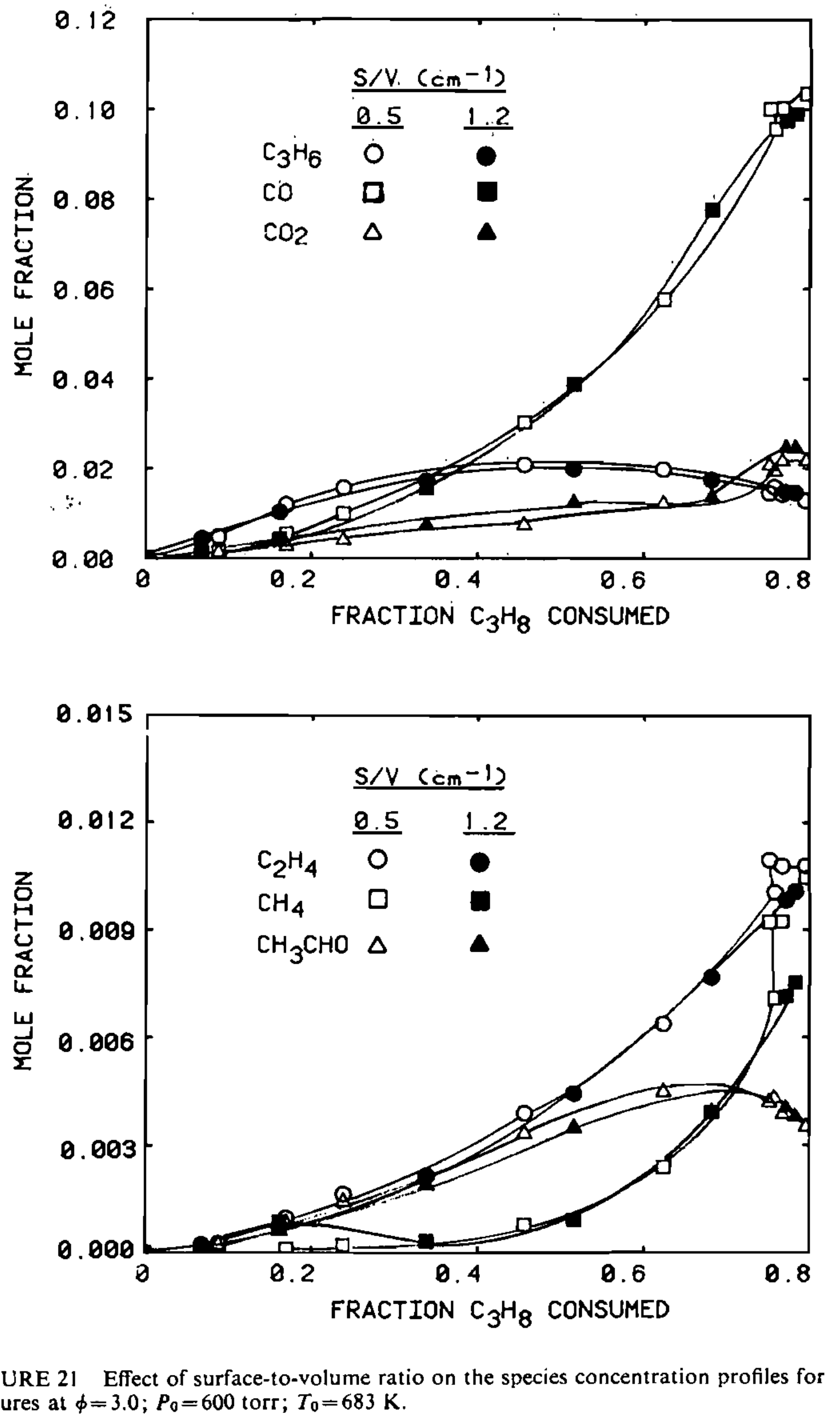

FIGURE 21 Effect of surface-to-volume ratio on the species concentration profiles for C_3H_8/air mixtures at $\phi = 3.0$; $P_0 = 600$ torr; $T_0 = 683$ K.

CHARACTERISTICS OF THE 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 in the Appendix. 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). 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 other kinetic models to lower temperatures.

Initiation and Radical Attack on the Fuel

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

$$C_3H_8 + O_2 \rightarrow C_3H_7 + HO_2. \tag{1}$$

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 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.

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, 1981) has shown that reactions of this type are rapidly reversible above 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.

Results of a recent study on the reaction of n-propyl radicals with O_2 (Slagle *et al.*, 1985) indicated the existence of a slightly different path responsible for the shift to the conjugate alkene and HO_2 as the products:

$$\begin{tikzcd}
C_3H_7 + O_2 \arrow[r, leftrightharpoons] & C_3H_7O_2^* \arrow[r] \arrow[d, "M"] & C_3H_6 + HO_2 \\
 & C_3H_7O_2. &
\end{tikzcd} \tag{6'}$$

In this mechanism, the formation of C_3H_6 and HO_2 occurs by this coupled reaction path and proceeds via an alternative decomposition route of the RO_2 radical rather than by the parallel-path bimolecular H-abstraction route [Reaction (6)]. Although the details of each of these mechanisms are different, overall, they both explain the turnover in the products with increasing temperature.

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:

$$RO_2 \rightarrow RCHO + RO. \tag{7}$$

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-$C_3H_7O_2$ radical will lead to these type products:

$$\text{i-}C_3H_7O_2 \rightarrow CH_3CHO + CH_3O. \tag{8}$$

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

$$CH_3CHO + O_2 \rightarrow CH_3CO + HO_2. \tag{9}$$

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:

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

$$C_3H_7O_2 + CH_2CHO \rightarrow C_3H_7OOH + CH_3CO, \tag{14}$$

$$C_3H_7OOH \rightarrow C_2H_7O + OH. \tag{15}$$

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; 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 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 (Figure 12). 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; 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 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 ($RC\dot{O}_3$) which is formed by O_2 addition to the acetyl radical. The acylperoxy radical can then abstract a hydrogen to form an acid:

$$RCO + O_2 \rightarrow RCO_3, \qquad (16)$$

$$RCO_3 \xrightarrow{+H} RCO_3H. \qquad (17)$$

Branching takes place as the acid decomposes into two radicals:

$$RCO_3H \rightarrow RCO_2 + OH. \qquad (18)$$

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

$$RCO + M \rightarrow R + CO + M, \qquad (19)$$

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

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 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:

$$RO_2 \rightarrow QOOH. \tag{20}$$

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

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

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:

$$C_3H_7O_2 \rightarrow C_3H_6OOH, \tag{22}$$

$$C_3H_6OOH \rightarrow C_3H_6O + OH, \tag{23}$$

$$C_3H_6OOH + O_2 \rightarrow O_2C_3H_6OOH, \tag{24}$$

$$O_2C_3H_6OOH \rightarrow HO_2C_3H_5O + OH, \tag{25}$$

$$HO_2C_3H_5O \rightarrow C_3H_5O_2 + OH. \tag{26}$$

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 is, however, much more important for longer chain (higher carbon number) alkanes.

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 unreactive NTC zone is again due to 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 propagating 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 hydrogen peroxide:

$$HO_2 \xrightarrow{+H} H_2O_2. \tag{27}$$

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 (Figures 6 and 7). The rate of hydrogen peroxide dissociation [Reaction (28)] is very low below 650 K, but increases rapidly at higher temperatures.

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

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. Therefore, the region between 600 and 650 K represents 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:

$$\text{n-}C_3H_7 + O_2 \rightarrow \text{n-}C_3H_7O_2, \tag{5a}$$

$$\text{i-}C_3H_7 + O_2 \rightarrow \text{i-}C_3H_7O_2, \tag{5b}$$

$$C_2H_5 + O_2 \rightarrow C_2H_5O_2, \tag{29}$$

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

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

$$\text{n-}C_3H_7OOH \rightarrow \text{n-}C_3H_7O + OH, \tag{31}$$

$$\text{i-}C_3H_7OOH \rightarrow \text{i-}C_3H_7O + OH. \tag{32}$$

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

$$\text{n-}C_3H_7O + O_2 \rightarrow C_3H_6O + HO_2, \tag{33}$$

$$\text{n-}C_3H_7O + O_2 \rightarrow CH_3CH_2CHO + HO_2, \tag{34}$$

$$\text{i-}C_3H_7O + O_2 \rightarrow CH_3CH_2CHO + HO_2, \tag{35}$$

$$\text{i-}C_3H_7O + O_2 \rightarrow CH_3COCH_3 + HO_2. \tag{36}$$

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

$$\text{n-}C_3H_7O \rightarrow C_2H_5 + HCHO, \tag{37}$$

$$\text{i-}C_3H_7O \rightarrow CH_3CHO + CH_3. \tag{38}$$

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

$$C_3H_6 + HO_2 \rightarrow C_3H_6O + OH. \tag{44}$$

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 are currently underway to examine the low temperature oxidation of propene (Wilk *et al.*, 1984).

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:

$$RO_2 + RO_2 \rightarrow ROOH + Q + O_2, \tag{45}$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2. \tag{46}$$

At higher temperatures it would involve reactions of HO_2:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \tag{47}$$

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

$$CH_3 + CH_3 \rightarrow C_2H_6, \tag{48}$$

$$C_2H_5 + C_2H_5 \rightarrow C_4H_{10}. \tag{49}$$

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

Heterogeneous termination results from the diffusion of radicals (RO_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 this paper where the added surface area slowed the reaction although it did not qualitatively or quantitatively alter the reaction products.

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 were 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 temperature rises of only 30 to 40 degrees.

Comparison to the High Temperature Mechanism

It is interesting to note the changes in the mechanism with temperature. It has been shown in this paper 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.

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 Figures 6 and 7. 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

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[a] (>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	$ROOH \rightarrow RO+OH$	$H_2O_2+M \rightarrow 2OH+M$	$H+O_2 \rightarrow OH+O$

[a] 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 800–900 K.

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:

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

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

while at higher temperatures the propyl radicals primarily decompose unimolecularly:

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

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

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

SUMMARY AND CONCLUSIONS

An experimental study of the low temperature oxidation of propane was carried out using a static reactor. A region of negative temperature coefficient was identified between 600 and 650 K. It was determined that this region represents a transition in the oxidation mechanism and separates a lower temperature reaction regime from an intermediate temperature reaction regime.

In the lower temperature regime (< 600 K), cool flames were observed and it was concluded that hydroperoxides are the main branching intermediates responsible for cool flame formation and acceleration of the reaction. Other branching agents believed to be important were also identified. These included aldehydes and peracids. Alkylperoxy radicals are the abundant radicals and oxygenated species are the major hydrocarbon products of the reaction.

In the intermediate temperature regime (> 650 K), hydroperoxyl radicals are abundant and hydrogen peroxide is the main branching intermediate. At these temperatures, the major hydrocarbon products consist of alkenes and alkanes. The change in the products and main branching route with temperature is due to the competition between reactions involving the addition of O_2 to alkyl radicals to form alkylperoxy radicals and reactions involving the abstraction of hydrogen from alkyl radicals by O_2 to form the conjugate alkene and the hydroperoxyl radical. The alkylperoxy radicals lead to the formation of hydroperoxides, which break down readily, while the hydroperoxyl radicals lead to the formation of hydrogen peroxide, which is stable below 650 K. This behavior leads to the negative temperature coefficient.

Examination of the effect of vessel surface area on the reaction showed that the induction period and overall reaction time was increased by the addition of surface. The reaction products, however, were virtually unaffected. From this study, it was concluded that the added surface did not affect the main reaction paths of the mechanism but did affect the reaction by increasing heterogeneous termination, which only slowed the overall rate.

Many of the intermediates formed in the reaction are highly reactive fuels. As they are formed from the initial 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. Therefore, any reaction mechanism which is to accurately describe the oxidation of propane must also take into account the reactions of the major intermediates.

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REFERENCES

Affleck, W. W., and Fish, A. (1967). Two-stage ignition under engine conditions parallels that at low pressures. *Eleventh Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 1003.

Aleksishvili, M. M., Polyak, S. S., and Shtern, V. Ya. (1974). Kinetics of the slow oxidation of propane. *Kinet. Catal.* **15**, 256.

Aleksishvili, M. M., Polyak, S. S., and Shtern, V. Ya. (1976). Mechanism of the oxidation of propane. *Kinet. Catal.* **17**, 958.

Baldwin, R. R., and Walker, R. W. (1973). Problems and progress in hydrocarbon oxidation. *Fourteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 241.

Baldwin, R. R., Plaistowe, J. C., and Walker, R. W. (1977). The mechanism of conjugate alkene formation and the importance of surface reactions in hydrocarbon oxidation. *Combust. Flame* **30**, 19.

Baldwin, R. R., Hisham, M. W. M., and Walker, R. W. (1984). Elementary reactions involved in the oxidation of propene: Arrhenius parameters for the reactions $HO_2 + C_3H_6 \rightarrow C_3H_6O + OH$. *Twentieth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh.

Bardwell, J. (1955). Cool flames in butane oxidation. *Fifth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 529.

Batt, L. (1979). The gas-phase decomposition of alkoxy radicals. *Int. J. Chem. Kinetics* **11**, 977.

Batten, J. J., and Ridge, M. J. (1955). *Aust. J. Chem.* **8**, 370.

Benson, S. W. (1965). Effects of resonance and structure on the thermochemistry of organic peroxy radicals and the kinetics of combustion reactions. *J. Amer. Chem. Soc.* **87**, 972.

Benson, S. W. (1976). *Thermochemical Kinetics.* Wiley, New York.

Benson, S. W. (1981). The kinetics and thermochemistry of chemical oxidation with application to combustion and flames. *Prog. Energy Combust. Sci.* **7**, 125.

Benson, S. W. (1982). Cool flames and oxidation: mechanism, thermochemistry and kinetics. *Oxidation Comm.* **2**, 169.

Bogan, D. J., Sanders, W. A., Wang, H. T., and Sheinson, R. S. (1983). Mechanism of excited formaldehyde formation in cool flames. Paper No. ESSCI 83-45, presented at the Fall Meeting of the Eastern States Section of the Combustion Institute, Providence, R.I.

Bonner, B. H., and Tipper, C. F. H. (1965). The cool flame combustion of hydrocarbons—II: Propane and n-heptane. *Combust. Flame* **9**, 387.

Burgess, A. R., and Laughlin, R. G. W. (1967). The role of hydroperoxides as chain branching agents in the cool-flame oxidation of n-heptane. *Chem. Comm.*, 769.

Cathonnet, M., Boettner, J. C., and James, H. (1981). Experimental study and numerical modeling of high temperature oxidation of propane and n-butane. *Eighteenth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, p. 903.

Dechaux, J. C. (1973). The negative temperature coefficient in the oxidation of hydrocarbons. *Oxidation and Combustion Reviews* **6,** 75.

Dechaux, J. C. (1981). Computer simulation of the slow oxidation alkanes. *Oxidation Comm.* **2,** 95.

Falconer, J. W., Hoare, D. E., and Savaya, Z. (1983). Peroxides in cool flames of isobutane. *Combust. Flame* **52,** 257.

Fish, A. (1964). Radical rearrangement in gas phase oxidation and related processes. *Quarterly Review* (*Chem. Soc., Lond.*) **18,** 243.

Fish, A. (1968). The cool flames of hydrocarbons. *Angew. Chemie* (*International Ed. in English*) **7,** 45.

Glassman, I. (1977). *Combustion.* Academic Press, New York.

Gray, B. F., and Felton, P. G. (1974). Low-temperature oxidation in a stirred-flow reactor—I: Propane. *Combust. Flame* **23,** 295.

Hautman, D. J., Dryer, F. L., Schug, K. D., and Glassman, I. (1981). A multiple-step overall kinetic mechanism for the oxidation of hydrocarbons. *Combust. Sci. Tech.* **25,** 219.

Jachimowski, C. J. (1984). Chemical kinetic reaction mechanism for the combustion of propane. *Combust. Flame* **55,** 213.

Kaiser, E. W. (1983). Propionaldehyde oxidation in the negative temperature coefficient region. *Int. J. Chem. Kinetics* **15,** 997.

Kaiser, E. W., Westbrook, C. K., and Pitz, W. J. (1984). Acetaldehyde oxidation in the negative temperature coefficient regime: experimental and modeling results. Paper No. WSSCI 84-89, presented at the Fall Meeting of the Western States Section of the Combustion Institute, Stanford, CA.

Knox, J. H., and Norrish, R. G. W. (1954). Low temperature oxidation and cool flames of propane. *Proc. Roy. Soc. Lond.* **A221,** 151.

LeFebvre, M., and Luquin, M. (1965). Les dernières étapes de l'oxydation lente du propane, Parts I and II. *J. de Chemie Phys.*, 775.

Lewis, B., and Von Elbe, G. (1961). *Combustion, Flames and Explosions in Gases.* Academic Press, New York.

Levitsky, A. A., Polyak, S. S., and Shtern, V. Ya. (1984). Mechanism of propane oxidation—mathematical modeling. *Int. J. Chem. Kin.* **16,** 1275.

McKay, G. (1977). The gas phase oxidations of hydrocarbons. *Prog. Energy Combust. Sci.* **3,** 105.

Minkoff, G. J., and Tipper, C. F. H. (1962). *Chemistry of Combustion Reactions.* Butterworths, London.

Mulcahy, M. F. R. (1947). Oxidation of lower paraffins. *Disc. Faraday Soc.*, No. 2, 128.

Newitt, D. M., and Thornes, L. S. (1937). The oxidation of propane, Parts I, II and III. *J. Chem. Soc. Lond.* 1656.

Nguyen Van Hai, Antonik, S., Sochet, L. R., and Luquin, M. (1970). Rôle des éthyléniques dans l'oxydation et la combustion des hydrocarbures satures. *Bull. Soc. Chim. France*, 2150.

Norrish, R. G. W. (1951). *Disc. Faraday Soc.* **10,** 269.

Ogorodnikov, I. A., Polyak, S. S., and Shtern, V. Ya. (1969). Mechanism of the oxidation of propane. *Kinet. Catal.* **10,** 998.

Pease, R. N., and Munro, W. P. (1934). The slow oxidation of propane. *J. Amer. Chem. Soc.* **56,** 2034.

Pease, R. N. (1938). The negative temperature coefficient in the rate of propane oxidation. *J. Amer. Chem. Soc.* **60,** 2244.

Pitz, W. J., and Westbrook, C. K. (1983). Chemical kinetics modeling of engine knock: preliminary results. Paper No. WSSCI 83-71, presented at the Fall Meeting of the Western States Section of the Combustion Institute, Los Angeles, CA.

Pollard, R. T. (1977). Hydrocarbons, in *Comprehensive Chemical Kinetics*, C. H. Bamford and C. F. H. Tipper (Eds.), Vol. 17. Elsevier, p. 249.

Salooja, K. C. (1965). The degenerate chain branching intermediates in hydrocarbon combustion: some evidence from studies on the isomeric hexanes. *Combust. Flame* **9,** 219.

Seakins, M. (1961). Peroxides and peroxy radicals in propane oxidation. *Proc. Roy. Soc. Lond.* **A261,** 281.

Shtern, V. Ya. (1964). *The Gas Phase Oxidation of Hydrocarbons.* Pergamon Press, London.

Slagle, I. R., Park, J-Y., and Gutman, D. (1985). Experimental investigation of the kinetics and mechanism of the reaction of n-propyl radicals with molecular oxygen from 297 to 635 K. *Twentieth Symposium* (*International*) *on Combustion*, The Combustion Institute, Pittsburgh, p. 733.

Tully, F. P., Ravishankara, A. R., and Carr, K. (1983). Kinetic study of the reactions of the hydroxyl radical with ethane and propane. *Int. J. Chem. Kinetics* **15,** 1111.

Walker, R. W. (1975). A critical survey of rate constants for reactions in gas-phase hydrocarbon oxidation. *Reaction Kinetics* **1,** 161.

Walker, R. W. (1977). Rate constants for reactions in gas-phase hydrocarbon oxidation. *Reaction Kinetics and Energy Transfer* **2,** 296.

Walsh, A. D. (1946). Progresses in the oxidation of hydrocarbon fuels—I. *Trans. Faraday Soc.* **42,** 269.

Walsh, A. D. (1947). Progresses in the oxidation of hydrocarbon fuels—II, III. *Trans. Faraday Soc.* **43,** 297, 305.

Warnatz, J. (1983). The mechanism of high temperature combustion of propane and butane. *Combust. Sci. Tech.* **34,** 177.

Westbrook, C. K., and Pitz, W. J. (1984). A comprehensive chemical kinetic mechanism for oxidation and pyrolysis of propane and propene. *Combust. Sci. Tech.* **37,** 117.

Wilk, R. D., Cohen, R. S., and Cernansky, N. P. (1982). 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 of the Combustion Institute, Livermore, CA.

Wilk, R. D., Cohen, R. S., and Cernansky, N. P. (1984). Low temperature oxidation of propene. Paper No. WSSCI 84-95, presented at the Fall Meeting of the Western States Section of the Combustion Institute, Palo Alto, CA.

Appendix

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	Est. this study[a]
$C_3H_8 + O_2 \rightarrow iC_3H_7 + HO_2$	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)
$C_3H_8 + HO_2 \rightarrow nC_3H_7 + H_2O_2$	8.47	0	14.9	Cathonnet *et al.* (1981)
$C_3H_8 + HO_2 \rightarrow iC_3H_7 + H_2O_2$	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 (1975)
$iC_3H_7O_2 + C_3H_8 \rightarrow iC_3H_7OOH + iC_3H_7$	9.0	0	17.1	Walker (1975)
$nC_3H_7O_2 + C_3H_8 \rightarrow nC_3H_7OOH + iC_3H_7$	9.0	0	17.1	Walker (1975)
$iC_3H_7O_2 + C_3H_8 \rightarrow iC_3H_7OOH + nC_3H_7$	9.0	0	19.4	Walker (1975)
$nC_3H_7O_2 + CH_3CHO \rightarrow nC_3H_7OOH + CH_3CO$	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)
$C_3H_6 + HO_2 \rightarrow C_3H_6O + HO_2$	9.02	0	14.2	Baldwin *et al.* (1985)
$CH_3CHO + O_2 \rightarrow CH_3CO + HO_2$	10.3	0	39.0	Walker (1975)

[a] 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. $\log_{10} 3$ was added to the pre-exponential to account for 3:1 ratio of primary to secondary C–H bonds.