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The auto-ignition of propane at intermediate temperatures and high pressures

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The results of a new experimental programme to measure auto-ignition delay times in mainly lean ($\phi = 0.5$) propane–air mixtures at intermediate temperatures in the range 850 K upwards and pressures 5–40 bar are described. The delays are compared to predictions obtained by the integration of two detailed chemical kinetic reaction schemes. Experimentally, a decrease in activation energy was observed at around 1000 K. The work shows that extrapolation of ignition delays obtained at high temperatures $T > 1000$ K can lead to significant overestimation of the actual delay times at lower temperatures. Despite the introduction of additional key reactions the kinetic schemes used could not fully reproduce the delay times observed experimentally at temperature below *ca.* 1000 K.

Introduction

Thermal auto-ignition delay times are an important parameter in many combustion applications. They reflect the controlling chemical processes in compression ignited engines and play a crucial role in high-pressure reactive shock and detonation phenomena. In addition, as many practical combustion systems are designed to provide controlled chemical reactions using suitable combustion technologies, situations can arise where unwanted auto-ignition may occur. For example mixing of the fuel and oxidant may take place at fairly high temperatures and pressures in the inlet manifold of a combustion chamber. If the auto-ignition delays are shorter than fuel/air residence time, ignition will occur in the manifold rather than as desired in the combustion chamber, with potentially disastrous effect. Auto-ignition is also the origin of 'knock' in spark ignited engines as a pocket of mixture, the 'end gas', is compressed and heated to auto-ignition before the main flame front arrives.

Auto-ignition delay times can vary over a wide range of timescales. A mixture heated by shock waves to temperatures in excess of 1200 K can react within a few microseconds whereas the same mixture at temperatures less than about 600–700 K may have an auto-ignition delay time of many seconds. Both of these temperature regions have been studied extensively in the past using a variety of techniques including, shock tubes,[1–6] rapid compression machines,[7,8] flow tubes[9–11] continuously stirred reactors[12–15] and static vessels.[16,17] Much relevant work on the lower temperature region is described in detail by various authors in the texts edited by Bamford[16] and by Pilling[17] and specifically for propane in the paper by Wilk.[18] However, many of the recent studies have been concerned with fuels of interest to the automotive industry. For other hydrocarbons the intermediate temperature region, $1000 > T/\mathrm{K} > 700$, has received less attention, primarily due to the difficulties in generating these temperatures over a timescale that is sufficiently short compared to the gas ignition delay time. Rapid compression machines can be used but these give a non-steady pressure–time history. An alternative is the flowing reactor[9–11] but it is expensive and technically challenging to achieve the high temperatures and pressures required.

High temperature ignition delays have been obtained routinely in studies using shock tubes, see for example the work of Burcat *et al.*,[1] Brown and Thomas,[2] Petersen *et al.*[3,4] Unlike rapid compression machines, shock tubes can generate high temperature conditions almost instantaneously, but there can be experimental difficulties in maintaining the shocked gas at the desired temperatures and constant pressures for the longer ignition delay times often prevalent at intermediate temperatures, although data has been obtained by Fieweger *et al.*[5] and Cierzki *et al.*[6] in this region.

In the present paper the results of a new experimental programme to measure auto-ignition delay times in propane–air mixtures in the intermediate temperature region ~850–1000 K and at pressures in the range 5–40 bar are described. Gas residence times as long as 6 ms have been obtained by using shock-tailoring techniques[19,20] to extend the duration of the constant temperature, pressure conditions behind the reflected shock. These measured auto-ignition delays could then be compared to predicted delay times obtained by integration of the mass and energy conservation equations derived from kinetics and thermochemistry using detailed kinetic schemes. The main motivation was to investigate whether changes in activation energy observed for diesel-type fuels and possibly a negative temperature coefficient (NTC) regime[5,6] for ignition delays, are obtained with a smaller hydrocarbon such as propane. Such changes in activation energies have been found in the temperature dependence of the propane oxidation rates[18] and in flow reactor results for the combustion of propane–air mixtures[11] where evidence of NTC behaviour was found. More recent work by Koert *et al.*[21] in lean propane–air mixtures ($\phi = 0.4$ where equivalence ratio ϕ = air/fuel ratio/stoichiometric air/fuel ratio) measured the products of propane oxidation in this intermediate temperature region and compared them to calculated values from their model. This work[21] did not calculate or measure ignition delays.

Previous studies

Ignition delay measurements

Previous experimental studies of the oxidation and auto-ignition of propane, as with other hydrocarbons, fall into three broad classes. Firstly those primarily concerned with the use of hydrocarbons to synthesise other materials or using sub-atmospheric glass systems.[16–18] These are usually static vessel investigations of the slower low temperature reactions (below 700 K) where reactions evolve over time of the order of seconds or greater. Secondly, those studies looking at more rapid reactions and that give auto-ignition times of the order of tens to hundreds of milliseconds at temperatures in the range 700–1100 K. These are usually observed in flow reactors, or in rapid compression machines. Finally, high temperature reactions where the auto-ignition delay times are less than 2 ms. Many of these experimental studies have been supported by parallel kinetic modelling activities.

Wilk *et al.*[18] undertook low temperature oxidation studies of propane–air from about 563 K upwards, and at initial pressures of 440–657 Torr and at equivalence ratios ϕ in the range 0.4–4.0 (although most work was with rich mixtures) using a static reactor. A transition region was observed between *ca.* 600–650 K which separated low temperature and intermediate temperature regimes. Over this latter temperature range the reaction rates exhibited a negative temperature coefficient. The reaction times used in these cases were of many hundreds of seconds duration. The authors do, however, mention another change in behaviour at temperatures in the range 900–1200 K into a still higher temperature region[18] (which may occur as low as 800 K in certain cases). The change in reaction behaviour was attributed to OH replacing HO_2 as the dominant species above this higher temperature boundary as the temperature increases, while in the regime below 700 K the main species was thought to be RO_2 (where R is C_3H_7 *etc.*). This third region, 900–1200 K is the one where this present investigation is concentrated.

Cathonnet *et al.*[22] used a flow reactor at temperatures near 1050 K at pressures of 1 and 6 atm to study propane–oxygen–nitrogen mixtures, at equivalence ratios ranging from 0.05 to 25, and monitored the product gas compositions using gas chromatography. A 100-step kinetic mechanism was also used to model the reaction behaviour observed experimentally. Hoffman *et al.*[23] extended the work of Cathonnet *et al.*[22] and used a flow reactor to study the non-isothermal reactions of propane–air at initial pressures of 3, 6 and 10 atm at initial temperatures of 850–900 K. For an equivalence ratio of 0.3 for propane–air and an initial pressure of 10 atm and temperature of 891 K some 50% of the fuel was consumed after 125 ms. These experiments are very similar to those reported by Lee *et al.*,[24] who also examined the effect of a platinum catalyst.

Lefebvre and coworkers[9,10] also used a flow reactor to study ignition delays in propane–air at equivalence ratios ranging from 0.2 to 0.7 with pressures in the range 1–10 atm and temperatures 670–1020 K. They observed clear dependences of ignition delay on gas temperature, with the ignition delays decreasing as the pressure increased. There is evidence that the rate of decrease in auto-ignition delay is reduced as the initial pressure is increased, an observation obtained at a fixed initial temperature of 908 K. They concluded that pressure exerted a fairly strong influence whilst that of fuel concentration was fairly weak. Lefebvre *et al.*[10] also noted that they had increasing difficulty in maintaining a stable auto-ignited flame at the higher pressures as the flame would flash back upstream but it is uncertain whether this was due to kinetic or turbulence effects. The ignition delays found in this work[9,10] are amongst the most relevant to the present effort and can be extrapolated to the region of this study but, as discussed later, do not agree with those presented here, possibly because of this stabilisation problem.

Steinberg and Kaskan[25] reported an early shock tube study of the auto-ignition in propane–air mixtures. They observed a lower temperature limit below which no ignition was observed of *ca.* 1000 to 1220 K, decreasing with pressure. The corresponding reflected shock pressures ranged from 7 to 20 atm. The longest delay times they noted were 470 μs, a limit probably set by the maximum operational time of the shock tube they used. Certain of their results do however show a trend towards a plateau in ignition delay times for temperatures just below 1200 K. Hawthorn and Nixon[26] also studied shock wave ignition of a range of hydrocarbon fuels. The minimum temperatures were again *ca.* 1050 K but some evidence of change in activation energy for temperatures in this region can be detected.

Burcat *et al.*[1] undertook shock tube studies to measure ignition delays in propane–oxygen–argon mixtures, including one lean mixture comparable to the propane–air mainly used in this work ($\phi = 0.5$) but with argon as diluent instead of nitrogen. Most of the measurements were taken over the temperature range 1250–1600 K and pressure 2.5–9.0 atm. The air-equivalent mixture was tested to temperatures as low as 1150 K and a clear decrease in the activation energy is visible when compared to the higher temperature studies. More recently Brown and Thomas[2] reported studies of the influence of nitrogen *vs.* argon as diluent and concluded that the influence of diluent was small.

Evidence of changes in activation energies and ignition delay behaviour with other hydrocarbons has been reported by Furutani *et al.*[27] and Petersen *et al.*[3,4] for methane and Hayashi and Takasu[28] for butane. Induction delay data obtained by these authors,[27,28] for both mixtures, was in good agreement with the data of Burcat *et al.*[1] at temperatures over 1200 K.

Kinetic predictions

Jachimowski[29] presented a study of a kinetic mechanism for modelling high temperature propane combustion reactions. The mechanism, which consisted of 27 reactions, gave good agreement with the experimental results of both Burcat *et al.*[1] and McLain and Jachimowski.[30] Both data sets were modelled over the temperature range 1150–2600 K. A distinction was made for the ignition delay behaviour with pressure and temperature between propane and hydrogen fuels. This may have implications for explosion development.

McLain and Jachimowski[30] predicted the variation in induction time as a function of initial pressures and temperatures for stoichiometric ($\phi = 1$) propane–air. At a temperature of 1000 K the induction delay was of the order of 5 ms at 10 atm reducing to *ca.* 1 ms at 50 atm. These calculations also showed clear indications that the activation energy changes significantly as the initial temperature is decreased below *ca.* 1200 K and the initial pressure is increased above 5 atm. This result is thus in qualitative agreement with the limited low temperature experimental data of Burcat *et al.*[1] and Myers and Bartle.[31] Experimental and kinetic modelling data on ignition delays in shock ignited propane and methane mixtures, have been presented by Frenklach and Bornside,[32] again for relatively high temperatures between 1330 K and 1600 K.

Dagaut *et al.*[12] successfully modelled the higher temperature experimental data obtained by Burcat *et al.*[1] A more extensive scheme was also compiled by Dagaut *et al.*,[14] and from this a more universal mechanism[15] was proposed. As this final 277 step kinetic scheme was first developed and validated against data obtained in a jet-stirred isothermal reactor and in shock tubes, this should have given some confidence in its ability to predict induction delay times in the intermediate temperature region of interest used in the present study. Brown and Thomas[2] found good agreement between their experimental ignition delays in air–propane mixtures at temperatures above 1200 K when using this newer scheme (Dagaut *et al.*[15]). They also note that it reproduced their data far better than the scheme proposed by Jachimowski.[29] Further modifications to the Dagaut scheme were reported recently by Voisin,[33] when he extended it to bigger molecules including kerosene. Recently a new modelling scheme for high pressure propane oxidation (10–15 atm) was used by Koert *et al.*[21] to compare experimental and predicted product analysis in a flow reactor between 600 and 800 K and indicated the presence of an NTC regime in propane oxidation in this region.

Experimental

Basic shock tube description

The present ignition delay measurements were made using a conventional shock tube arrangement. The circular cross-section test section had a total length of 3.75 m and an internal diameter of 64 mm. A 3.00 m long stainless steel high pressure driver section was separated from the main test section by Mylar diaphragms. To ensure reproducible shock speeds a double diaphragm bursting mechanism was used, where gas at an intermediate pressure to the driver and test pressures was contained in a small volume formed between two sheets of Mylar of suitable thickness. When this intermediate pressure was vented the pressure differences developed caused both diaphragms to rapidly rupture allowing the incident shock wave to form itself rapidly and reproducibly.

Test gas mixtures were prepared by first evacuating a mixing vessel, and then introducing the required molar quantities of the constituent gases, and were controlled by the method of partial pressures. A Trans Instruments Series 2000 pressure transducer matched with a Newport INFCS indicator was used to measure the pressures to an accuracy of ± 0.5 mbar or $\pm 0.05\%$ for a mixture at atmospheric pressure. After filling, the homogeneity of the gaseous mixture was ensured by allowing it to mix by diffusion overnight. The nitrogen and oxygen gases used were BOC Commercial Grade and the propane was technical grade with a maximum purity of 99.5%. A limited number of tests with high purity propane ($>99.5\%$) gave very similar results to the lower purity propane.

Instrumentation

A Kistler pressure transducer located in the closed end wall of the test section was used to record the normal shock reflection pressures. In addition, two PCB pressure transducers with their sensing surfaces flush to the inner tube wall were located 170 and 90 mm from the end wall. Pressure histories obtained from these three transducers were used to monitor incident and reflected shock pressures as well as the development of any combustion wave. Incident shock velocities measured from these pressure histories were also used to calculate the temperature and pressure behind the reflected shock *via* the usual method with the Chemkin programme.[34]

Flush mounted quartz windows were located next to the end wall and 90 mm upstream to provide optical access and allow light emission to be monitored *via* fibre optic cables connected to Hamamatsu R647 head-on type photomultipliers. Narrow band filters were used to selectively monitor emission from CH* radicals at 430 nm. The emission and pressure signals were captured by a multi-channel transient 10 MHz recorder triggered by a signal from a fourth PCB pressure transducer upstream.

Tailored shock waves

The extension of ignition delay measurements using shock tubes into the region 800–1100 K depends on the lengthening of the available time in the reflected shock under reasonably well characterised conditions using tailoring techniques. These techniques have been used for many years in a different form[35,36] (often with the use of dump tanks) in single pulse shock tubes. As we have found the application of tailoring techniques significantly increases the times available and hence allows the range of experimental temperatures investigated to be extended downwards, it is useful to specify the background to its use in more detail, as this technique is not well known.

In a one-dimensional shock tube the quiescent initial test gas, (region 1) in Fig. 1, is first compressed by the incident shock wave, IS, and increasing the pressure, density, temperature and sound speed. The temperature, pressure and density of the driver gas, region 4, will, however, have decreased, as the rarefaction wave RHW propagates back through it. The boundary between the test gas, region 2, and the expanded driver gas, region 3, is referred to as the contact surface, CS. The pressures and flow velocities across any contact surface are equal but the densities and temperature are different in the modified test and driver gases.

The incident wave reflects from the closed end and the reflected shock, RS, now propagates back upstream, heating the test gas further to the reflected shock temperature and the gas behind an ideal reflected shock is essentially stationary. This reflected wave can interact with the contact surface and, if there is an acoustic mismatch, additional waves TS and AD can arise as a result of this interaction and can be either expansion or compression type. These propagate both upstream and downstream. When the downstream disturbance AD passes through the stationary gas sitting at reflected gas conditions it will perturb this gas, both in temperature and pressure, thus limiting the useful measurement time for ignition delay studies to τ_1. The maximum possible observation time τ_2 for gas near the end wall, is the time from the reflection of the incident shock to the arrival of the reflected expansion wave, RRW, from the driver end. Such time is a function of the tube length. If the unwanted acoustic disturbance AD or TS at the contact surface is eliminated by acoustic matching, this procedure is known as *tailoring* and the observation time can be prolonged up to a maximum of τ_2.

For an acoustic impedance, the coefficient of reflection, A_r is given by

$$A_r = \frac{\rho_3 c_3 - \rho_2 c_2}{\rho_3 c_3 + \rho_2 c_2} \quad (1)$$

To minimise A_r then $\rho_2 c_2 = \rho_3 c_3$ (across the contact surface), where ρ is the density and c the local gas velocity of sound (subscripts 2 and 3 refer to gas on either side of CS).

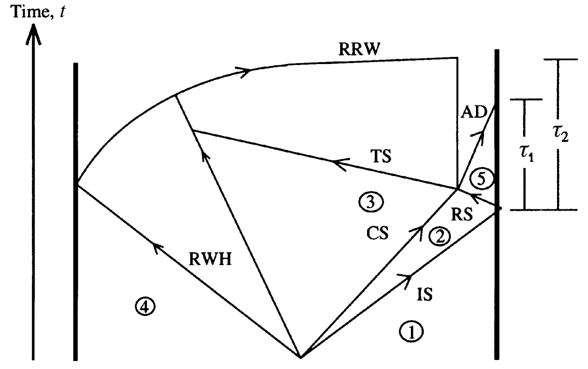

Fig. 1 Sketch of typical wave interaction diagram in a closed shock tube. IS, incident shock, RHW, head of rarefaction wave; CS, contact surface; RS, reflected shock; TS, transmitted shock; AD, reflected acoustic discontinuity; RRW, reflected expansion wave. Regions 1, initial test gas; 2, shocked incident gas; 3, driver gas after expansion; 4, initial driver gas; 5, gas after shock reflection. Observation times: τ_2 maximum theoretical; τ_1 limited by wave interaction at contact surface.

To achieve the test pressure and temperatures required for the present study, helium gas was used as the primary driver gas when air was used as the test gas. In practice, unwanted gas dynamic interactions described above can be virtually eliminated if a small quantity of argon is added to the helium driver. Estimates of the optimal driver gas composition required to fully tailor for specific reflected shock conditions in an arbitrary test gas mixture were easily found using a spreadsheet analysis, programmed with the appropriate gas dynamic equations for adiabatic expansion of the driver gas and shock compression of the test gas. In this way, by iterating on the driver gas properties *e.g.* pressure, sound speed, density and ratio of principal specific heats, initial conditions that caused eqn. (1) to be satisfied could be found. Tailoring the shock tube in this manner eliminates the production of any pressure or rarefaction waves, thus extending the duration of uniformity of the conditions of the test gas behind the reflected shock (and before combustion) and thus allowing reactions with longer ignition delays at lower temperatures to be studied. Blank gas tailoring experiments were carried out under each condition (with the hydrocarbon replaced by an inert gas) before any ignition delay measurements were made. All pressure records were inspected and those exhibiting occasional pressure transients were rejected. Such tests gave an indication of the maximum possible delay time observable under those experimental conditions and were confirmed by pressure profiles of the actual fuel–air mixtures used. With the present tube length, the maximum observation times up to 6 ms could be obtained *via* this method (compared to 2–3 ms without tailoring), while in other tubes in our laboratory, times up to 9 ms could be achieved—the longer the tube the longer the time obtainable.

Between 3% and 10% of argon in helium was required to produce tailored shocks into mixtures of 2.1% C_3H_8–20.6% O_2–77.3% N_2 but 10% to 17% of argon in the helium for mixtures of 0.8% C_3H_8–8.0% O_2–91.2% Argon. The percentage of argon required was found to increase with decreasing incident shock Mach numbers (and hence temperature).

Experimental results

Comparison of ignition delays with previous high temperature data

Before proceeding to lower temperature studies using the shock tube described above, it appeared prudent to repeat some previous measurements by other workers. In practice, little data at temperatures less than 1200 K were found, with the exception of the one series reported by Burcat *et al.*[1]

An increase in pressure was used as the criterion for identifying the onset of ignition as this corresponds to the release of energy and, as will be shown later, this correlated well with the onset of emission from CH* radicals, except at the lowest temperatures where emission preceded the pressure rise. This latter effect has been found by other workers[3–5] and reflects the low rates of heat release under these conditions during the early stages of combustion, which may be likened to 'cool flame' conditions or other similar pre-combustion phenomena. The onset of ignition was determined by extrapolating back the pre-ignition pressure–time profile and the pressure due to the increase occurring from the exothermic combustion until they intersected. A maximum error in this determination could be estimated at $\leqslant 10\%$ in the delay time.

The first mixture studied in the present work was 0.8% C_3H_8–8.0% O_2–91.2% Ar, fuel/oxygen equivalence ratio $\phi = 0.5$, for a reflected shock pressure of 5 bar which corresponds to the 2A mixture studied by Burcat *et al.*[1] Arrhenius plots of the ignition delay measurements results from both studies are shown in Fig. 2. The highest temperature data from this work agrees with the lowest temperature data of Burcat *et al.*[1]

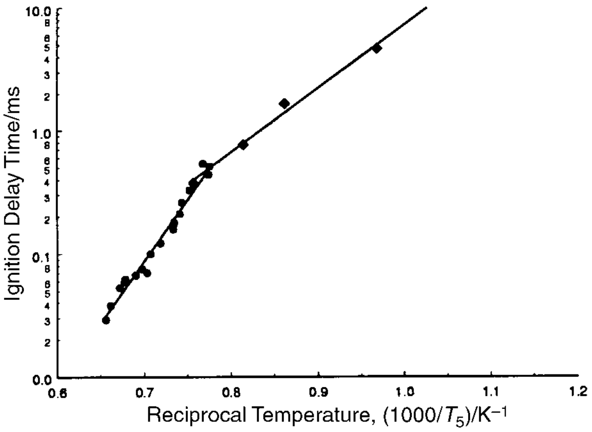

Fig. 2 Measured ignition delay times for 0.8%C_3H_8–8.0%O_2–91.2%Ar, $\phi = 0.5$. (●) Burcat *et al.*,[1] (◆) present data. Reflected shock pressure 5 bar.

The high temperature data of Burcat[2] gives an activation energy of 192 kJ mol^{-1}, whereas the intermediate temperature data from the present work gives 108 kJ mol^{-1} with a standard error of about 7 kJ mol^{-1}. The data are consistent with a change in activation energy occurring at *ca.* 1290 K.

In the present work ignition delay data for the stoichiometric mixture $\phi = 1$ was also measured, 4.0% C_3H_8–20.2% O_2–75.8% Ar and this is plotted in Fig. 3 for a reflected shock pressure of 5 bar and is seen to be in reasonable agreement with the high temperature measurements of Burcat *et al.*,[1] at a pressure of 7 bar. In the present work data in the intermediate temperature range gave an activation energy of about 38 kJ mol^{-1} compared with the 156 kJ mol^{-1} obtained by Burcat *et al.*[1] for the higher temperature range. We have analysed our data in terms of two regions of different activation energies rather than a polynomial curve based upon similar data for other fuels such as methane and ethane which shows this effect more clearly.[3 7] Petersen *et al.* also found such a change[3] in methane oxidation.

Ignition delays at intermediate temperatures

The majority of tests undertaken during the present study used mixtures of propane–air with a fuel/oxygen equivalence ratio, $\phi = 0.5$. Auto-ignition delay measurements were made for several reflected shock pressure and temperatures ranges.

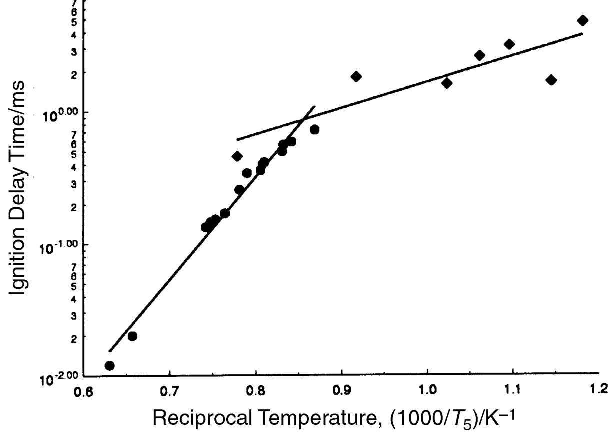

Fig. 3 Measured ignition delay times 4.0%C_3H_8–20.2%O_2–75.8%Ar, $\phi = 1.0$. (●) Burcat *et al.*,[1] pressure 7 bar; (◆) present data, pressure 5 bar.

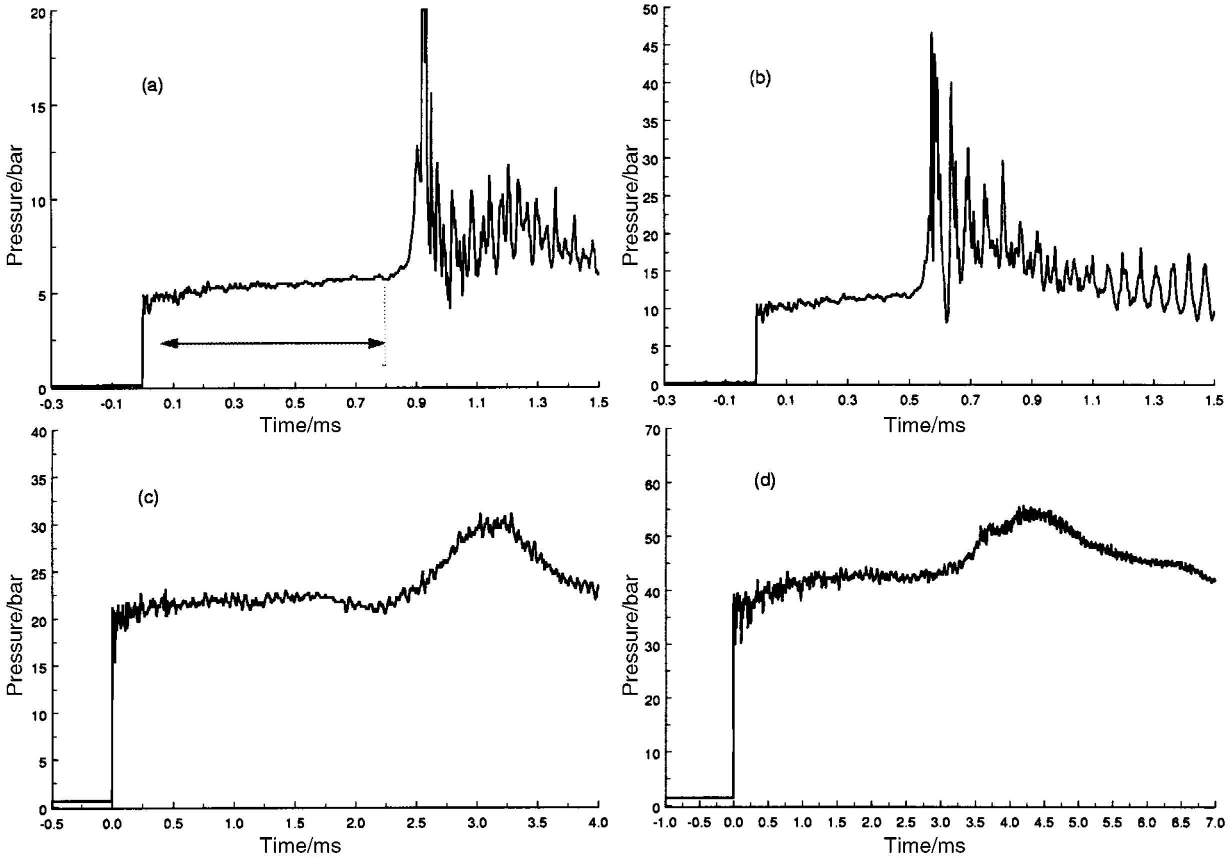

Fig. 4 Typical pressure histories obtained for 2.1%C_3H_8–20.6%O_2–77.3%N_2, $\phi = 0.5$. (a) P_5 4.72 bar, T_5 1195 K; (b) P_5 10 bar, T_5 1195 K; (c) P_5 21 bar, T 979 K; (d) P_5 40 bar, T 886 K.

Typical pressure histories measured from the Kistler gauge located in the end plate are shown in Fig. 4.

The time $t = 0$ was taken as the instant when the incident shock wave reflects from the closed end wall. Fig. 4(a) and (b) are pressure histories for reflected shock pressures of 4.72 and 10 bar respectively. The reflected gas temperature was calculated to be 1195 K for both tests. Both show a rapid increase in pressure due to the rapid energy release at this high temperature. This type of combustion can be called strong as against the milder type shown in Fig. 4(c) and (d). The auto-ignition delay, given by the onset of pressure rise, decreased from *ca.* 0.8 to 0.5 ms as a consequence of doubling the reflected shock pressure, other parameters remaining the same.

For a reflected shock pressure of 21 bar when the reflected gas temperature was decreased to 979 K only mild pressure increases were observed (Fig. 4(c)) A similar pressure history obtained at reflected shock pressure and temperature of 40 bar and 886 K (Fig. 4(d)) where the auto-ignition delay is of the order of 2.9 ms.

As the combustion went from mild to strong it was found to develop at the higher temperatures into a detonation for a number of experiments at 5 and 10 bar. For safety reasons it was necessary to avoid such detonations, so the higher pressure data was confined to the intermediate temperature range below about 1100 K.

A comparison of pressure and CH* emission from a test at a reflected shock pressure and temperature of 10 bar and 1205 K is possible from Fig. 5(a). The emission ignition delay measurements were often more imprecise than the pressure ones, particularly at the lower temperature end with a smaller intensity emission often preceding the main one. It was felt that the pressure ignition delay, which was related to the temperature increase due to combustion and heat release was a better measure of the start of the main combustion and was used for delay measurements.

Fig. 5(b) and (c) illustrate the nature of the variations in light emission signals observed as the reflected gas temperature was decreased.

Table 1 Summary of derived activation energies for the mixture 2.1% C_3H_8–20.6% O_2–77.3% N_2 and 4.0% C_3H_8–20.2% O_2–75.8% argon ($\phi = 1$) for different temperature and pressure ranges

Reflected shock pressure P_5/bar$_a$	Temperature range T_5/K	E/kJ mol^{-1}	Standard error/ kJ mol^{-1}	log(A/s)	Standard error in log(A/s)
5($\phi = 1$)	850–1280	38	10	−4.74	0.18
5($\phi = 0.5$)	998–1357	108	9	−4.94	0.13
10($\phi = 0.5$)	1122–1278	113	19	−5.23	0.10
10($\phi = 0.5$)	933–1057	52	9	−5.32	0.08
20($\phi = 0.5$)	835–1012	48	6	−5.27	0.07
40($\phi = 0.5$)	847–935	58	3	−5.96	0.02

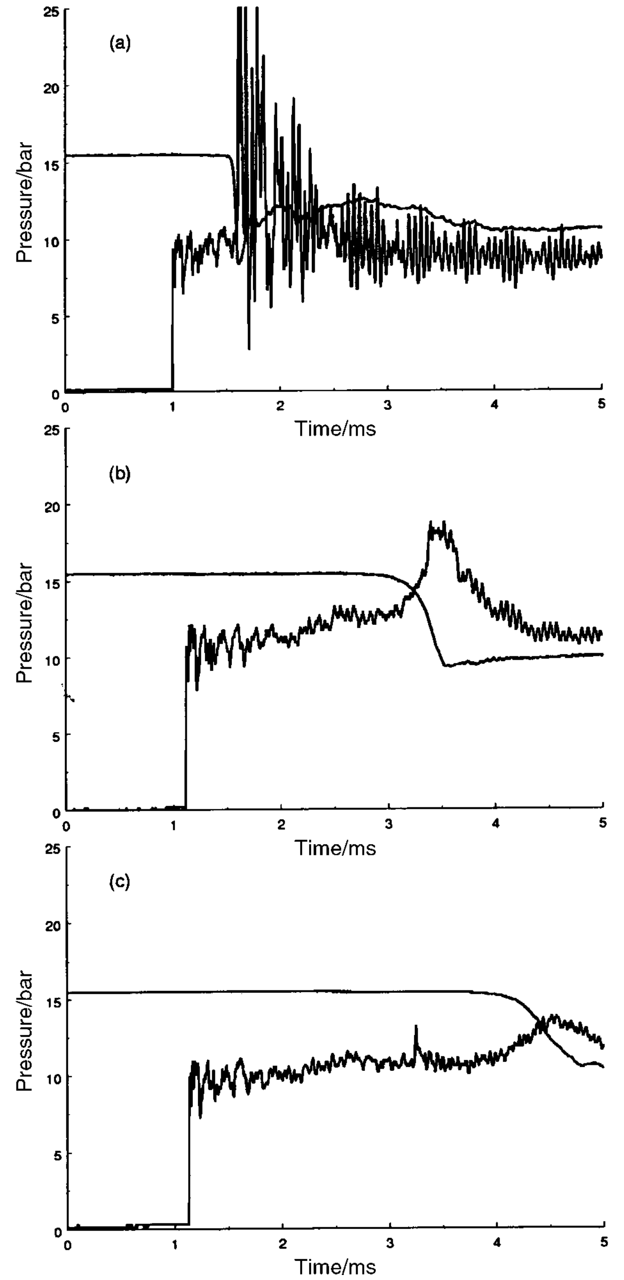

Fig. 5 Typical photo-multiplier outputs and pressure histories obtained for 2.1%C_3H_8–20.6%O_2–77.3%N_2, $\phi = 0.5$. (a) P_5 8 bar, T_5 1205 K; (b) P_5 10.0 bar, T_5 1025 K; (c) P_5 10.2 bar, T_5 996 K.

The ignition delays observed at reflected shock pressures of 5, 10, 20 and 40 bar are plotted in Fig. 6. Only representative points are shown for the 40 bar line. A number of experiments were done at $\phi = 0.6$. This change in stoichiometry from 0.5 to 0.6 reduced the ignition delays by about a factor of 2 at a pressure of 40 bar.

Activation energies and pre-exponential constants for ignition delays, t_{ign} shown in Fig. 2 and 6 (expressed in Arrhenius form $t_{\text{ign}}/\text{s} = A\ \exp(E/RT)$) are listed in Table 1 where E = activation energy in kJ mol^{-1} and log A gives the constant factor with A in seconds, T the temperature and R the universal molar gas constant. The errors given are one standard deviation.

Kinetic predictions of ignition delays

In addition to the direct measurement of auto-ignition delays with propane mixtures reported in the preceding section, delays were also computed from basic chemical kinetic reaction mechanisms using the CHEMKIN v 3.5 software routines, after Kee *et al.*[34] Data for rate coefficients can be obtained from Baulch *et al.*[38] The SHOCK and SENKIN programs were used together with reaction mechanisms reported previously by Jachimowski[28] and Dagaut *et al.*[12,14,15]—modified by Voisin.[33] The Voisin[33] mechanism has been validated previously in the ranges $1 \leqslant P/\text{atm} \leqslant 15$, $0.15 \leqslant \phi \leqslant 4$, $900 \leqslant T/\text{K} \leqslant 1200$ and was also extended later to higher temperatures, $(1200 \leqslant T/\text{K} \leqslant 1700)$. The Jachimowski[29] scheme was validated for the high temperature range $1150 \leqslant T/\text{K} \leqslant 2600$ and pressure in the range $0.5 \leqslant P/\text{atm} \leqslant 50$. Both mechanisms were enhanced by the addition of the reactions in the standard Chemkin format listed in Table 2.

Computed auto-ignition delays obtained with the original three schemes, based on an increase in CH* concentration, for the mixture 0.8% C_3H_8–8.0% O_2–91.2% Ar, $\phi = 0.5$ at a reflected shock pressure of 5 bar are plotted in Fig. 7. The experimental data is given as solid symbols and theoretical calculations as open symbols. Neither scheme is very good at reproducing the experimental data.

Ignition delays were predicted for the propane–air mixture of 2.1% C_3H_8–20.6% O_2–75.8% N_2 (stoichiometry $\phi = 0.5$), for reflected shock pressures of 5 and 10 bar and these are shown in Fig. 8(a) and (b). The experimental results exhibit a clear difference in activation energy for the high and intermediate temperature range. The kinetic predictions from both schemes on the other hand do not show a sufficient change in

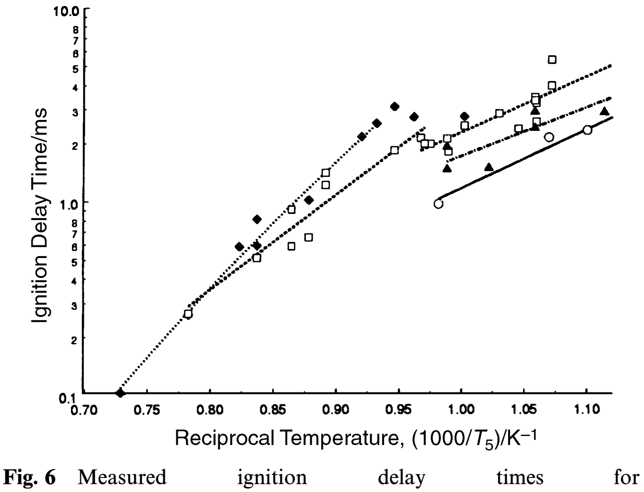

Fig. 6 Measured ignition delay times for 2.1%C_3H_8–20.6%O_2–77.3%N_2, $\phi = 0.5$. Test pressures: (◆) 5 bar; (□) 10 bar; (▲) 20 bar; (○) 40 bar.

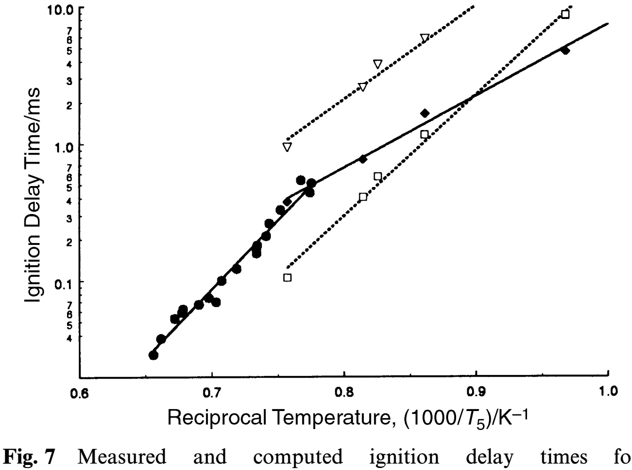

Fig. 7 Measured and computed ignition delay times for 0.8%C_3H_8–8.0%O_2–91.2%Ar, $\phi = 0.5$. (●) Burcat *et al.*,[1] (◆) present data, (▽) modified Dagaut,[14] (□) modified Jachimowski.[29] Solid lines, experimental; broken lines, calculated. Reflected shock pressure 5 bar.

Table 2 Additional reactions added to reaction schemes[a]

Reaction	A	n	E/J
$H + O_2 + N_2 \Leftrightarrow HO_2 + N_2$	2.60E+19	−1.24	0.00
$CH_3 + OH \Leftrightarrow CH_2O + H_2$	8.00E+12	0.0	0.0
$CH_3 + O_2 \Leftrightarrow CH_3OO$	1.70E+60	−15.1	78 387
$C_2H_5O \Leftrightarrow CH_2O + CH_3$	1.00E+15	0.0	90 400
$CH_3O + HO_2 \Leftrightarrow CH_2O + H_2O_2$	1.20E+13	0.0	0.0
$CH_3O + CH_3 \Leftrightarrow CH_2O + CH_4$	2.41E+13	0.0	0.0
$CH_3OOH \Leftrightarrow CH_3O + OH$	6.46E+14	0.0	179 895
$CH_3OO + CH_3 \Leftrightarrow CH_3O + CH_3O$	3.00E+13	0.0	−5021
$CH_3OO + H_2O_2 \Leftrightarrow CH_3OOH + HO_2$	2.40E+12	0.0	41 597
$CH_3OO + CH_2O \Leftrightarrow CH_3OOH + HCO$	2.00E+12	0.0	48 798
$CH_3OO + CH_4 \Leftrightarrow CH_3OOH + CH_3$	1.80E+11	0.0	77 300
$C_2H_5 + O_2 \Leftrightarrow C_2H_5O_2$	1.00E+12	0.0	0
$C_2H_5O_2 + CH_2O \Leftrightarrow C_2H_5O_2H + HCO$	2.00E+12	0.0	48 798
$C_2H_5O_2H \Leftrightarrow C_2H_5O + OH$	1.00E+16	0.0	179 816

[a] $k = AT^n \exp(-E/RT)$, with E in J and A in mol cm^3 s^{-1} units.

ignition delays at these intermediate temperatures to reproduce the changes in activation energies observed experimentally. The predicted activation energies are still similar to those obtained in the experiments at higher temperatures. The Dagaut[14] mechanism over-predicts the absolute delay times whereas the Jachimowski[29] scheme under-predicts them to an even greater extent. A similar discrepancy between experimental observations and kinetic predictions of ignition delay time was found at the other reflected shock pressures as well, see Fig. 9(a) and (b).

The agreement between experimental and predicted delay times at higher temperatures was much better than that found in the intermediate temperature region.

Sensitivity analysis

The results of a sensitivity analysis on the mechanism of Voisin[33] are shown in Fig. 10 and 11 for pressures of 5 and 10 bar respectively, and different temperatures.

At temperatures of around 750 K the main production route of HO_2 is

$$R + O_2 \Rightarrow \text{alkene} + HO_2$$

either occurring directly or *via* intermediate species such as R′COOH.

The HO_2 radical is less reactive than OH radical and the HO_2 concentration increases to allow the reaction below to

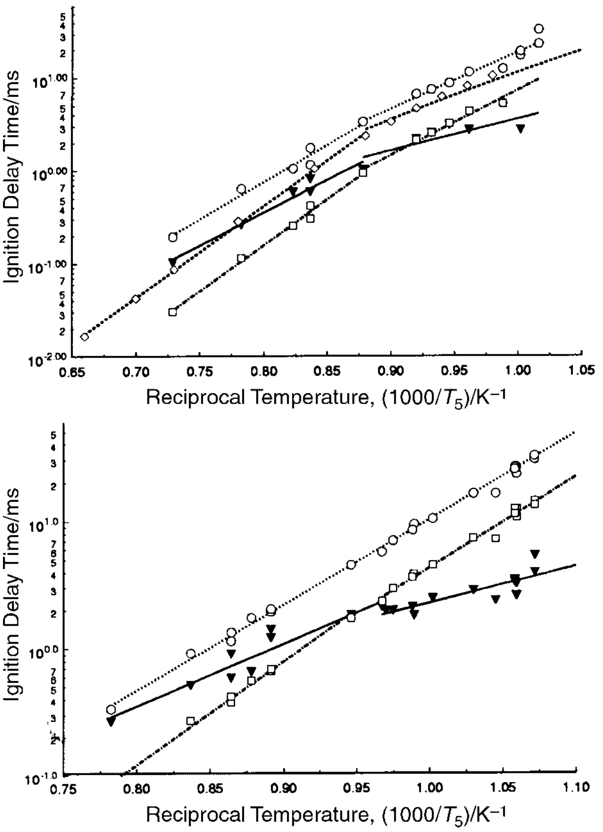

Fig. 8 Comparison of measured (closed symbols, solid line) and predicted (open symbols, broken line) auto-ignition delay times for propane–air mixture, equivalence ratio 0.5 at 5 and 10 bar. (□) Jachimowski scheme,[29] (○) Voisin scheme,[33] (◇) Dagaut scheme.[14] (▼) Experimental (a) 5 bar, (b) 10 bar.

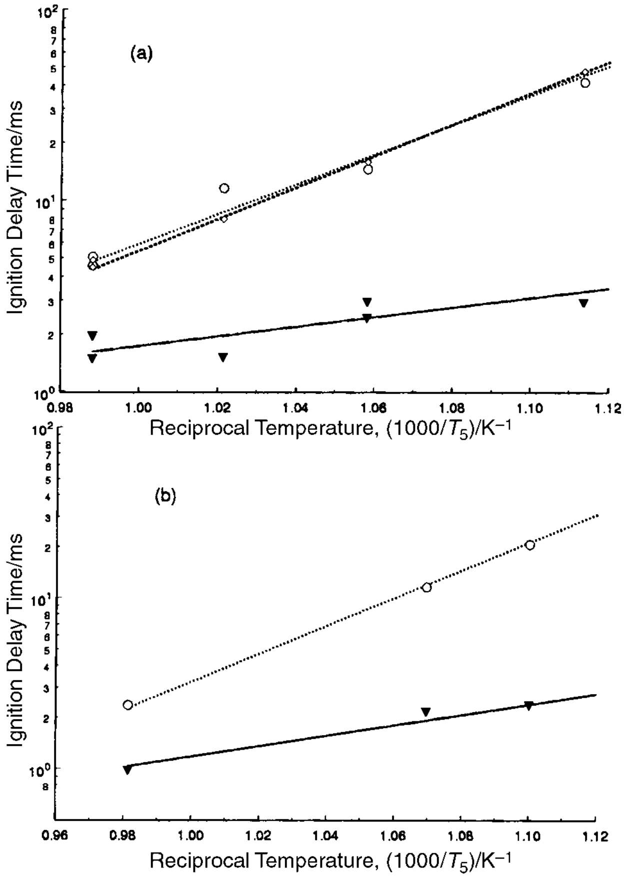

Fig. 9 Comparison of measured (closed symbols solid lines) and predicted (open symbols, broken lines) auto-ignition delay times for propane–air mixture, equivalence ratio = 0.5. (○) Voisin scheme,[33] (◇) Dagaut scheme.[14] (▼) Experimental (a) 5 bar, (b) 40 bar.

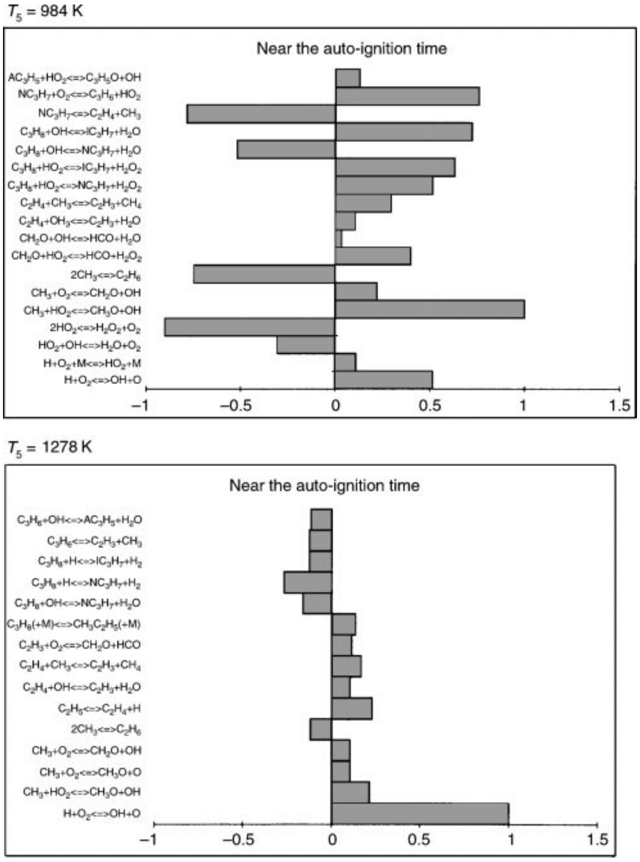

Fig. 10 Results of sensitivity analysis using SENKIN of reaction (*i*) *vs.* $\delta T/\delta a_i$ where a_i is the mass fraction of *i* for the mixture 2.1% C_3H_8–20.6% O_2–77.3% N_2, $P_5 = 5$ bar, $\phi = 0.5$. Results obtained with the mechanism of Voisin.[33]

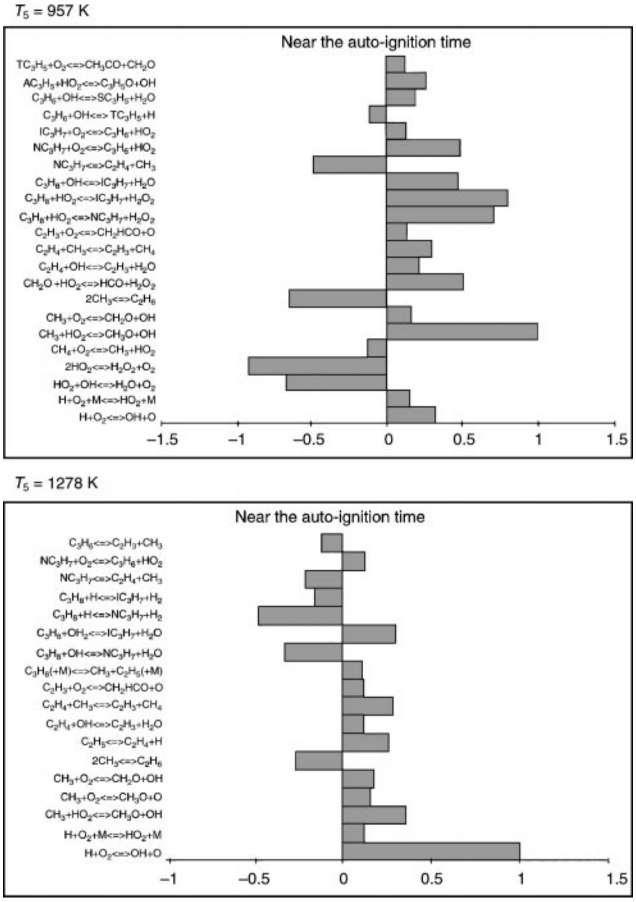

Fig. 11 Results of sensitivity analysis using SENKIN of reaction (*i*) *vs.* $\delta T/\delta a_i$ where a_i is the mass fraction of *i* for the mixture 2.1% C_3H_8–20.6% O_2–77.3% N_2, $P_5 = 10$ bar, $\phi = 0.5$. Results obtained with the mechanism of Voisin.[33]

become important:

$$HO_2 + HO_2 \Rightarrow H_2O_2 + O_2.$$

At temperatures of 957 and 984 K, H_2O_2 is also produced by

$$RH + HO_2 \Rightarrow R + H_2O_2$$

and OH is produced from H_2O_2 by collisions with inert species

$$H_2O_2 + M \Rightarrow 2\,OH + M.$$

At higher temperatures ($T \geqslant 1200$ K) the rate of formation of the alkenes and the HO_2 radical is smaller than at intermediate temperatures and the reaction

$$H + O_2 + M \Rightarrow HO_2 + M$$

(at the same temperature and typical pressures) is slower than the reaction:

$$H + O_2 \Rightarrow OH + O.$$

The latter reaction becomes the main route for the production of OH radicals under these conditions and, therefore, for causing auto-ignition of the fuel.

The other reaction $H + O_2 + M \Rightarrow HO_2 + M$ becomes more important as the pressure increases. Another possible source of H_2O_2 is *via* the reactions:-

$$C_3H_8 + HO_2 \Leftrightarrow i\text{-}C_3H_7 + H_2O_2$$

$$C_3H_8 + HO_2 \Leftrightarrow n\text{-}C_3H_7 + H_2O_2.$$

The main source of OH radical should be the homogeneous decomposition of H_2O_2 at intermediate temperatures, but the sensitivity analysis indicates that the reaction

$$CH_3 + HO_2 \Leftrightarrow CH_3O + OH$$

is also significant.

The latter reaction was added following the findings of Hunter *et al.*[39] who suggested that this reaction has a large influence on the pre-ignition chemistry in shock-initiated methane oxidation at intermediate temperatures.

The sensitivity analysis shows the importance some other reactions involving propane consumption, mainly reactions with OH radicals:

$$C_3H_8 + OH \Leftrightarrow n\text{-}C_3H_7 + H_2O$$

$$C_3H_8 + OH \Leftrightarrow i\text{-}C_3H_7 + H_2O$$

$$C_3H_8 + H \Leftrightarrow n\text{-}C_3H_7 \quad \text{or } i\text{-}C_3H_7 + H_2$$

and from the propyl radical decomposition:

$$n\text{-}C_3H_7 \Leftrightarrow C_2H_4 + CH_3.$$

Dagaut *et al.*[12,14] have underlined the increasing influence of propane reactions with hydroperoxyl radicals with increasing pressure

$$C_3H_8 + HO_2 \Leftrightarrow n\text{-}C_3H_7 + H_2O_2$$

$$C_3H_8 + HO_2 \Leftrightarrow i\text{-}C_3H_7 + H_2O_2.$$

From these results, it appears that propane is mainly converted to propyl radicals.

This is related to the increased concentration of hydroperoxyl radicals with the pressure caused by the fact that the rate of the reaction (efficiencies of M are taken as in Baulch[38] with that of N_2 and O_2 being the same):

$$H + O_2 + M \Leftrightarrow HO_2 + M$$

becomes larger than that of branching reaction:

$$H + O_2 \Leftrightarrow OH + O.$$

We can see this result when we compare the data in Fig. 9 for temperatures of 984 and 957 K at 5 and 10 bar.

The results shown in Fig. 7–9 indicate that the Dagaut,[14] Voisin[33] and Jachimowski[29] mechanisms, even when modified by the extra reactions given above, do not reproduce the ignition delays found experimentally.

Conclusions

Experimental measurements in the intermediate temperature region have shown that autoignition delays in lean propane–air mixtures, at an equivalence ratios of 0.5, lead to shorter ignition delay times than expected based on an extrapolation of delay data obtained at temperatures in excess of 1200 K or of lower temperature data obtained from flow system data. A reasonable agreement was obtained between measured delays and those predicted using a detailed chemical kinetics scheme for temperature greater than 1200 K. A sensitivity analysis has demonstrated the importance of the hydroperoxyl, propyl and methyl radicals at temperatures in the range $1100 > T/K > 850$ but the modified schemes were still not able to account fully for the observed changes in activation energy at these intermediate temperatures.

Our overall conclusion is that changes in activation energy are obtained at temperatures in the range 850–1100 K, a region of practical interest in combustion devices and also explosion development. Some present kinetic schemes dangerously over-predict auto-ignition delay times in this temperature regime. Further work is required to improve the overall mechanisms and check rate data for certain key reactions.

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