Comprehensive Kinetic Model for the Low-Temperature Oxidation of Hydrocarbons

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The low-temperature oxidation chemistry of linear and branched alkanes is discussed with the aim of unifying their complex behavior in various experimental systems using a single detailed kinetic model. New experimental data, obtained in a pressurized flow reactor, as well as in batch- and jet-stirred reactors, are useful for a better definition of the region of cool flames and negative temperature coefficient (NTC) for pure hydrocarbons from propane up to isooctane. Thermochemical oscillations and the NTC region of the reaction rate of the low-temperature oxidation of n-heptane and isooctane in a jet-stirred flow reactor are reproduced quite well by the model, not only in a qualitative way but in terms of the experimental frequencies and intensities of cool flames. Very good agreement is also observed for fuel conversion and intermediate-species formation. Irrespective of the experimental system, the same critical reaction steps always control these phenomena. The results contribute to the definition of a limited set of fundamental kinetic parameters that should be easily extended to model heavier alkanes.

Introduction

The oxidation chemistry in the low- and intermediate-temperature regimes (600–900 K) is important and plays a significant role in the overall combustion process. Autoignition in diesel engines as well as end-gas autoignition and knock phenomena in s.i. engines are initiated at these low temperatures (Cernansky et al., 1986). In the low-temperature regime the oxidation of hydrocarbons is a very complex process, involving different propagation and chain branching reactions. These reactions can lead to a large variety of phenomena. Slow combustion and the negative temperature dependence of reaction rate (NTC) are wholly kinetic in origin. Oscillatory cool-flame, single-, two-stage, and multistage ignitions are consequences of the interactions of kinetics and heat release. The ignitions can occur in adiabatic conditions, while cool flames require heat losses. This chemistry has been recently reviewed by Griffiths (1995), but there is still a need for better characterization of the reactivity of hydrocarbon fuels in the low-temperature regime.

Recently, major research efforts have been undertaken at Drexel University (Koert et al., 1994; Anand, 1994; Anand et al., 1994; McCormick, 1994; Wood, 1994) and Princeton University (Kowalski et al., 1991; Vermeersch et al., 1991; Callahan, 1995) in pressurized flow reactors (PFR) to supply new and relevant experimental data. Jet-stirred flow-reactor (JSFR) (Dagaut et al., 1994, 1995) and rapid-compression machine (RCM) studies (Minetti et al., 1994, 1995; Griffiths et al., 1993) as well as explosion diagrams and cool-flame behavior from static reactors (SR) add new information to the kinetic mechanism.

From pioneering works (Lignola and Reverchon, 1987; Gray, 1990), significant efforts have also been devoted to observing the dynamic behaviors of high-molecular-weight hydrocarbon–air mixtures in JSFR operating in conditions close to those occurring in s.i. engines (D'Anna et al., 1992; Cavaliere et al., 1993; Ciajolo et al., 1993). The ability to repro-

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duce the amplitudes and frequencies of oscillation is a rigorous criterion for the test of kinetic models.

As clearly stated in the literature (Westbrook and Dryer 1984; Griffiths, 1995), to demonstrate the robustness of a model, the validation of kinetic mechanisms should span as many different types of practical systems and as wide a range of conditions as possible, and the model particularly must be able to reproduce the wide variety of phenomena that accompany low-temperature oxidation.

Reaction Classes and Kinetic Parameters

Recently a general approach for the development, validation, and extension of a detailed oxidation scheme was presented (Ranzi et al.,1995a). The primary reactions involved in the low-temperature oxidation of hydrocarbon fuels have been classified and large reaction schemes have been automatically generated. As the carbon number of the molecule rises, the detailed reaction scheme becomes very complex. The number of isomers of the same homologous class of molecules and radicals increases, as does the number of reactions. In these cases properly lumping procedures, both for reactions and components, becomes very useful. These lumped mechanisms of heavy species consist of a limited number of equivalent reactions that are then coupled with a very detailed scheme for the oxidation of C_1-C_4 species. Only a few fundamental kinetic parameters are needed for the progressive extension of the scheme toward heavier species (Chevalier et al., 1992; Westbrook and Pitz, 1993; Curran et al., 1995). Figure 1 represents a convenient simplification of the primary oxidation mechanism of alkanes, and it also shows the main classes of propagation reactions. A sensitivity analysis shows that all these classes are needed to describe the complete variety of oxidation phenomena. This primary propagation mechanism is very similar to those of Cox and Cole (1985) and Hu and Keck (1987), both of which were derived from the Shell model (Halstead et al., 1977), but there are at least two major differences. These models account for the effect of different hydrocarbons by adjusting the rate parameters of the isomerization reaction of alkylperoxy radicals on the basis of experimental data. In the present case, rather like in the unified approach by Griffiths et al. (1994), the rate parameters of the proposed model for the different hydrocarbons (Figure 1) is directly obtained from the detailed kinetic scheme without the need of experimental information (Ranzi et al., 1995a). Moreover, by using the detailed submechanism of C_1-C_4 oxidation, the proposed approach allows a proper description of the successive fates of the primary products with a better evaluation of heat release.

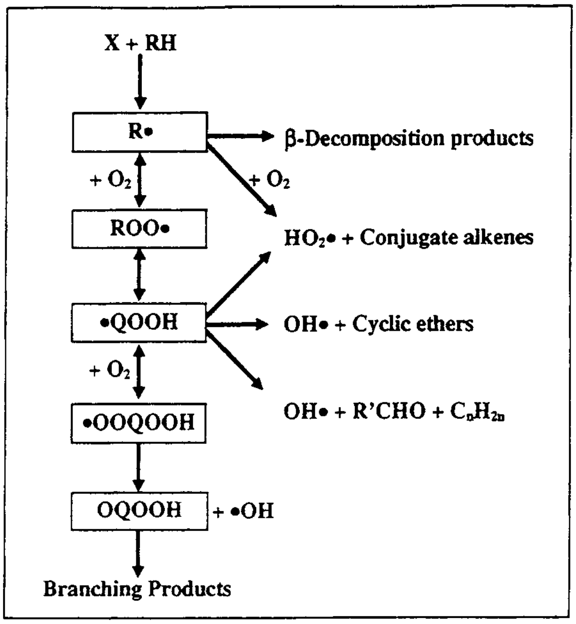

Figure 1. Kinetic scheme of the primary oxidation reactions of *n*-alkanes.

The resulting kinetic model of hydrocarbon oxidation from methane up to isooctane is constituted of about 150 species involved in 3,000 reactions. Once comparison with the experimental data has been done for several different species (starting from propane, which is the simplest fuel exhibiting the typical low-temperature phenomena, up to isooctane), then it is appropriate to verify, and eventually to modify, the original kinetic assumptions.

In the low-temperature regime fuel consumption occurs via H-atom abstraction, primarily by OH· and HO_2·, and to a lesser extent by H·, CH_3· and O_2. The rate constants are calculated with analogous rules discussed elsewhere (Ranzi et al., 1994).

The alkyl radical can interact with molecular oxygen to form conjugate alkenes and HO_2·. Tsang and Hampson (1986) suggest an A-factor of 2.0E+8 (L/mol s for H atom) with an activation energy of 3,000 (cal/mol). To reproduce the experimental distribution of trimethyl-pentenes in isooctane oxidation we assumed that O_2 does not show different selectivities toward different H types (Ranzi et al., 1997). That is why the same activation energy for primary, secondary, and tertiary H atoms has been assumed. Different kinetic studies (McAdam and Walker, 1987; Bozzelli and Dean, 1990; Wagner et al., 1990) indicate that alkenes are formed through a complex path involving an excited $ROO\cdot^{*}$, and these kinetic parameters require more investigation. Thus, Westbrook and Pitz (1993) assume that the direct channel does not proceed at low temperature, but they include these reactions only in the high-temperature mechanism.

The alkyl radicals can also add with O_2 to produce an alkyperoxy radical ROO·. The transition between low- and high-temperature mechanisms is determined by the equilibrium $R\cdot + O_2 \leftrightarrow ROO\cdot$. Addition with O_2 is assumed to have the same bimolecular rate of 1.5E+9 (L/mol s), while the reverse decomposition has a rate of 3.0E+13 exp $(-30{,}000/RT)$ (s^{-1}).

H-atom abstraction of hydrocarbon species from ROO· to produce alkyl-hydroperoxides is of minor importance, and hydroperoxide formation is essentially due to recombination reactions with HO_2·.

The most important step for the ROO· species is the isomerization to the hydroperoxyalkyl radical (·QOOH) via an internal H atom transfer. A more in-depth description of this type of reaction was given before (Ranzi et al., 1995a). Taking recommendations in the literature into account (Benson, 1976; Baldwin et al., 1982; Westbrook et al., 1991; Bozzelli and Pitz, 1994), the activation energy depends on the type of H atom being abstracted and on the ring size of the transition state. The A-factor is assumed to be lower with increasing ring size due to the loss of internal rotors. Similar considerations can also be used to evaluate the reverse isomerization reaction of hydroperoxyalkyl radicals.

The ·QOOH radicals can react via four major pathways. The radicals that have a radical site in the α position to the hydroperoxy group can decompose to yield a conjugate alkene and $HO_2\cdot$ with a rate of $3.0E+13 \exp(-23{,}000/RT)$ (s^{-1}) (Baldwin et al. 1986; Slagle et al., 1984; Bozzelli and Dean, 1990). At low temperature, this is the prevailing path to conjugate alkenes.

·QOOH species with a radical site in the β position can undergo β-scission, forming smaller olefins and aldehydes. Similar to Pollard (1977) a rate of $5.0E+13 \exp(-24{,}500/RT)$ (s^{-1}) is chosen. Another reaction path of ·QOOH species is the O–O homolysis, producing OH· radicals and cyclic ethers. The five-membered ring tetrahydrofuran species have the lowest ring strain energy, while the oxiran species have the highest. Activation energy for these reactions is believed to range from 10,000 to 17,000 (cal/mol). Pyrans are disregarded since the eight-membered-ring transition state for the peroxy isomerization is not considered.

At low temperature, ·QOOH can add molecular oxygen to form hydroperoxy–alkylperoxy radicals (·OOQOOH) with the same bimolecular rate previously reported for the addition of O_2 to alkyl radicals. All these competitive reaction channels for ·QOOH radicals play an important role in the correct characterization of the NTC region. The relative values of the kinetic parameters for the different reaction paths are more important for the correct prediction of product distribution and reactivity than their absolute values.

The ·OOQOOH radicals can decompose back to ·QOOH or can isomerize, forming OH· and ketohydroperoxide species (OQOOH). The rates of this isomerization, via internal H-atom transfer, are analogous to those for ROO· ↔ ·QOOH isomerization. However, the activation energy is decreased when the H atom being abstracted is bound to a C atom substituted by a hydroperoxy group. Finally, the decomposition of ketohydroperoxides, which leads to the formation of a carbonyl radical and OH·, is considered. A rate of $5.0E+14 \exp(-43{,}000/RT)$ is chosen (Sahetchian et al., 1982, 1991).

The appearance of an induction period followed by something suddenly happening within the kinetic model is essentially a combination of three factors:

- The rate of decomposition of ketohydroperoxides, which are very strongly temperature-dependent
- The competition of nonbranching reactions in the formation of ketohydroperoxides through the R·/ROO·/·QOOH chain
- the exothermicity of the oxidation process.

Table 1 summarizes the range of proposed kinetic parameters for the elementary propagation reactions of alkane oxidation. As we already mentioned, the kinetic parameters for the equivalent reactions shown in Figure 1 are directly derived from the detailed kinetic schemes of the different species.

Comparison with Experimental Data

This overall kinetic scheme has been validated over a broad range of operating conditions pertaining to the low- and intermediate-temperature regimes, and explains the main reaction features in the various experimental devices.

This analysis shows that a simple low-temperature mechanism, assembled with a unified set of reaction assumptions, can explain different sets of experimental data obtained in flow reactors (PFR and JSFR) and static reactors (SR and RCM). Only a few comparisons are here reported, even if the model has also been extensively proved in terms of intermediate species.

Pressurized Flow Reactor

A key advantage of flow reactors is that the temperature, pressure, and residence-time history of the reactant gas mixture are well characterized and controlled. The pressurized flow reactor (PFR) system used to generate the present data consists of a 2.5-cm-diameter Vycor reactor housed in a stainless-steel pressure vessel, designed to operate at pressures up to 20 atm and at temperatures up to 1,000 K. The experimental system has been described in detail before (Koert and Cernansky, 1992; Koert et al., 1994). Two types of experiments have been carried out. In controlled-cooldown (CCD) experiments, residence time is held constant and tem-

Table 1. Kinetic Parameters for the Main Propagation Reactions of Alkane Oxidation

Main Propagation Reactions	Reference Kinetic Parameters (Units: 1, cal, mol, s)	
	A	Ea
$R\cdot \rightarrow$ β-decomposition products	$3.0E+13$	28,000 ÷ 32,000
$R\cdot + O_2 \rightarrow ROO\cdot$	$1.5E+09$	0
$ROO\cdot \rightarrow R\cdot + O_2$	$3.0E+13$	30,000
$R\cdot + O_2 \rightarrow$ conjugate alkenes $+ HO_2\cdot$	$2.0E+08$ *	3,000
$ROO\cdot \rightarrow \cdot QOOH$	$4.0E+10 \div 6.2E+11$ *	20,000 ÷ 28,500
$\cdot QOOH \rightarrow ROO\cdot$	$1.2E+10 \div 1.8E+11$	12,000 ÷ 19,100
$\cdot QOOH \rightarrow$ conjugate alkenes $+ HO_2\cdot$	$3.0E+13$	23,000
$\cdot QOOH \rightarrow OH\cdot +$ cyclic ethers	$2.0E+10 \div 4.0E+11$	7,000 ÷ 20,000
$\cdot QOOH \rightarrow OH\cdot + R'CHO + CnH_2n$	$3.0E+13$	24,500
$\cdot QOOH + O_2 \rightarrow \cdot OOQOOH$	$1.5E+09$	0
$\cdot OOQOOH \rightarrow \cdot QOOH + O_2$	$3.0E+13$	30,000
$\cdot OOQOOH \rightarrow OQOOH + OH\cdot$	$4.0E+10 \div 6.2E+11$ *	18,000 ÷ 26,000
$OQOOH \rightarrow$ branching products	$5.0E+14$	43,000

*Per H atom.

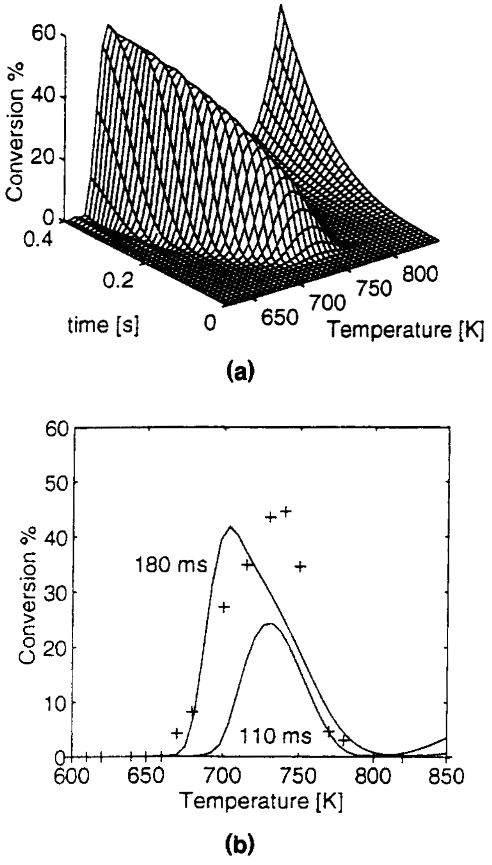

Figure 2. n-Butane oxidation ($nC_4H_{10}/O_2/N_2$ 0.54/11.70/87.76) in a pressurized flow reactor at 5 atm.

(a) Calculated fuel conversion as a function of inlet temperature and residence time; (b) comparison between experimental (+) (Anand, 1994) and calculated (−) n-butane conversion. Experimental data refer to 110-ms residence time.

perature is slowly varied, while in constant-inlet-temperature (CIT) experiments, the temperature is held constant and the residence time is varied. The CCD experiments produce a rapid reactivity map that provides guidance for selecting appropriate conditions for the more traditional time-evolution CIT experiments (Wilk et al., 1989; Koert et al., 1992). In either case, samples of the reacting gases are withdrawn with a glass-lined, water-cooled gas-sampling probe. Stable species are identified and quantified using both an on-line FTIR system and GC/FID and GC/MS techniques. Typically, experimental results give information on fuel conversion and on product formation.

Only a sample of experimental data is presented in Figure 2, where panel (a) is a complete map of calculated conversion of n-butane as a function of temperature and contact time and panel (b) shows the comparison with experimental data. These predictions have been obtained in adiabatic conditions. Similar results have also been observed assuming an isothermal reactor. At the experimental residence time of 110 ms, a lower conversion is predicted. To obtain the measured conversion the model requires longer residence time, which also shifts the NTC region to lower temperatures. This feature indicates that the location of the NTC region depends on system severity in addition to being a function of the ceiling temperature, where alkyl and peroxyl radicals have similar concentrations (Benson, 1981).

The observed product distributions confirm that NTC is a result of the relative importance of the low- and intermediate-oxidation paths. At low temperatures, the reaction rate is accelerated by the formation of two OH· and oxygenated species resulting from successive O_2 additions to ·QOOH. As the temperature increases, formation of conjugate alkenes and HO_2· from ·QOOH reduces the system reactivity.

A very similar effect should be observed for all the hydrocarbons. Data, obtained in a pressurized flow reactor, on n-heptane and isooctane oxidation are discussed and compared elsewhere (Callahan et al., 1996).

Isothermal Jet-Stirred Flow Reactor

Extensive studies of diluted hydrocarbon oxidation have been conducted in an isothermal JSFR (Dagaut et al., 1994, 1995). The effect of pressure and contact time on n-heptane conversion is reported in Figure 3. The apparent reduction of the NTC, as well as the shift of this region, can be mainly explained on the basis of the higher contact time. As a matter of fact, the NTC region should move toward higher temperatures when pressure increases, as is clearly shown by shock-tube experiments (Ciezki and Adomeit, 1993; Ranzi et al., 1995b).

Rapid Compression Machine

The autoignition of hydrocarbons is studied conveniently in RCMs (Griffiths et al., 1993; Minetti et al., 1994, 1995), where fuel concentration is closer to the operating conditions of internal combustion engines. These experiments severely test the model. Total and first-ignition delay times of n-butane are reported in Figure 4 (Minetti et al., 1994). At low temperatures the two-stage ignition mechanism and the NTC behavior involving the accumulation and subsequent decomposi-

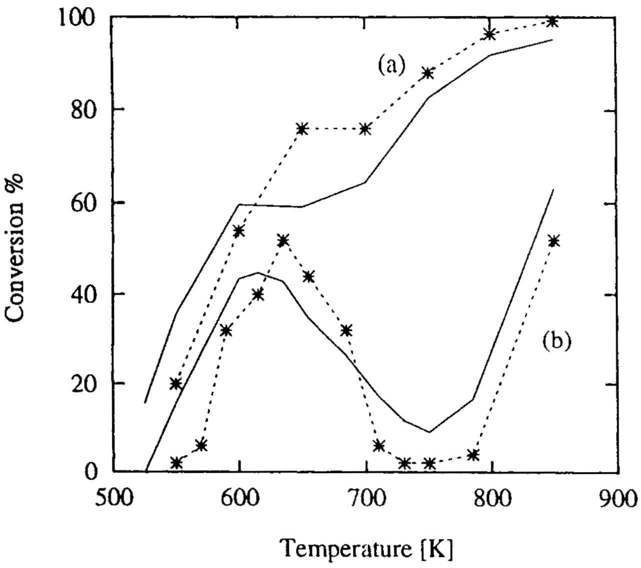

Figure 3. Oxidation of 0.05% n-heptane ($\Phi = 1$) in a JSR.

Comparison between experimental (- - - -) (Dagaut et al., 1994, 1995) and calculated (——); conversions at (a) 40 atm and 2-s contact time, (b) 10 atm and 0.5-s contact time.

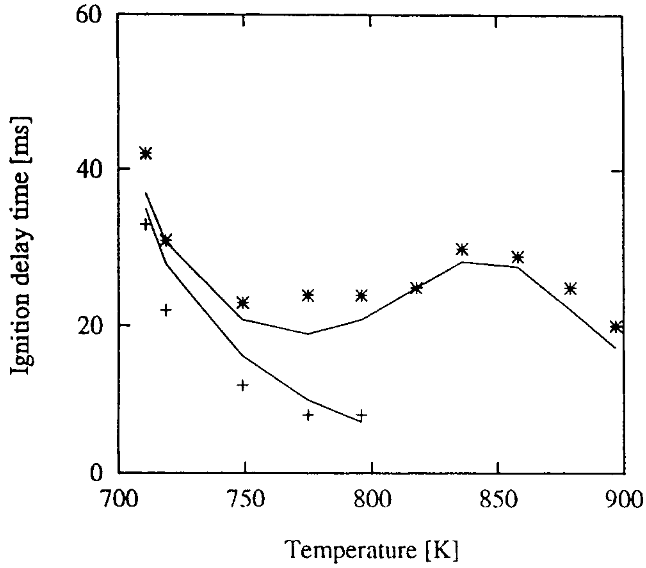

Figure 4. First ignition (+) and total delay times (*) for the oxidation of a stoichiometric *n*-butane/air mixture in a RCM.

Comparison between experimental (+) (Minetti et al., 1994) and calculated (——) data.

tion of ketohydroperoxides are observed and correctly reproduced. The temperature of the system during the first ignition, equivalent to a cool flame, reaches 850–900 K. Due to the practical adiabaticity of RCM, this temperature is maintained and a second induction time is needed to activate the high-temperature mechanism. At high temperatures the ignition becomes single stage although the NTC region disappears only when temperature exceeds 850 K. Figure 5 reports different calculated temperature profiles for *n*-butane oxidation that clearly indicate the transition from two-stage to single-stage ignition and the NTC region. It is important to observe that the modeling assumption of an adiabatic system is well verified during the compression stroke though it requires more attention in the postcompression period (Griffiths et al., 1993). Similar criticism is needed for the assumed spatial uniformity of the system (Minetti et al., 1994, 1995).

Static Reactor

Propane, propene, and *n*-butane oxidation have been studied by Wilk et al. (Wilk et al., 1986, 1987, 1995) in a conventional nonisothermal batch SR. The system consists of a cylindrical Pyrex vessel (volume 1,395 cm^3, diameter 10 cm, surface-to-volume ratio 0.5 cm^{-1}) located inside a temperature-controlled compartment. Reactants are first premixed and then rapidly admitted to the preheated, evacuated reaction vessel. At a selected time during the course of the reaction, a portion of the reactor's contents is withdrawn into an evacuated sampling loop, quenching the reaction. Stable species are identified and measured using GC/FID and GC/MS techniques. Temperature, pressure, and detailed species evolution profiles were obtained for a number of equivalence ratios and initial temperatures and pressures. The data indicate the NTC and multiple cool-flame regimes and provide a wealth of results for developing and validating mechanisms.

The model predictions for propane oxidation are in good agreement with the experimental data (Wilk et al., 1986) and do a good job of reproducing the transition from dumped cool flames to slow combustion, as is clearly shown in Figure 6. Good agreement with experimental results has also been obtained in terms of species evolution, as reported in Figure 7. At intermediate temperature, the model properly predicts a higher formation of propylene as a result of ·QOOH decomposition. CH_3OH profiles indicate the dominant presence of oxygenated compounds from the ketohydroperoxide decomposition at lower temperatures.

Another temperature evolution during propane oxidation is examined in Figure 8. When the inlet temperature is raised,

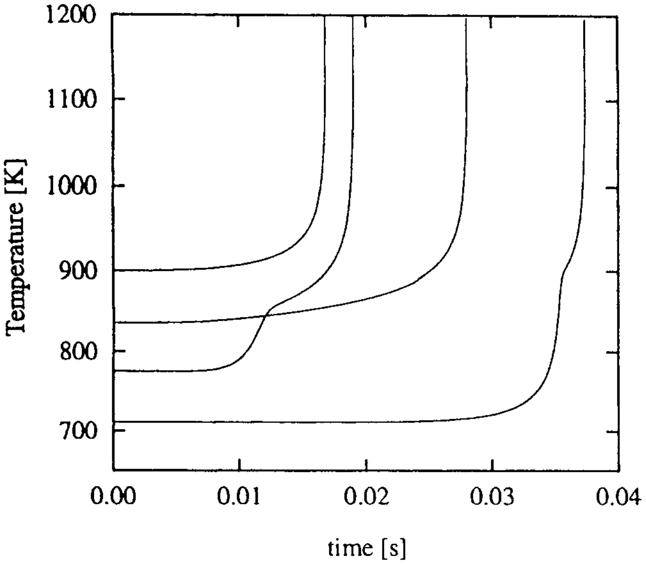

Figure 5. Predicted temperature profiles of a stoichiometric *n*-butane/air mixture in an RCM.

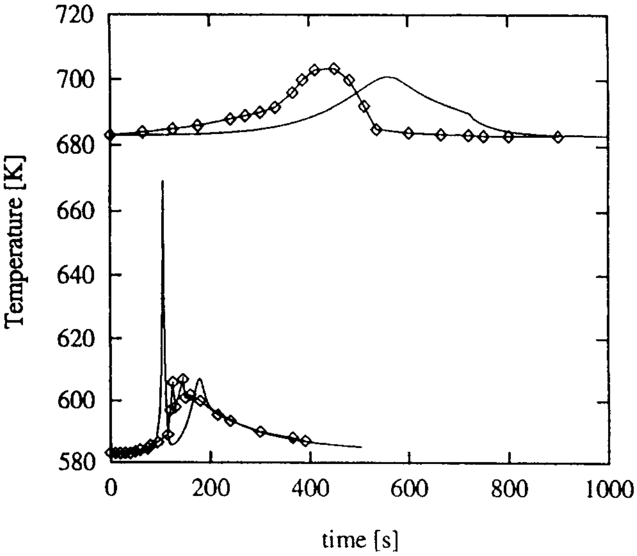

Figure 6. Oxidation of propane/air mixtures (Φ = 3) at 583 torr in a static reactor.

Comparison between experimental (◇) (Wilk et al., 1986) and calculated (——) temperature profiles.

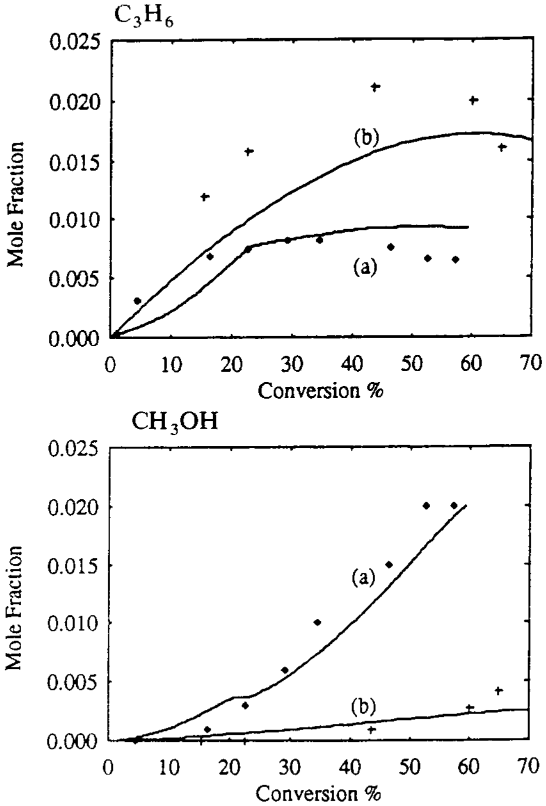

Figure 7. Oxidation of propane/air mixtures ($\Phi = 3$) at 583 torr in a static reactor at 583 (a) and 683 K (b).

Comparison between experimental (♦, +) (Wilk et al., 1986) and calculated (——) CH_3OH and C_3H_6 profiles.

the system moves from slow combustion to cool flames, back to slow combustion, and finally to ignition. Induction times show the NTC region. The analysis of these data permits definition of the ignition boundaries. Explosion diagrams, already available in the literature (Newitt and Thornes, 1937; Pollard, 1977), can also contribute to a better definition of the overall scheme (Ranzi et al., 1995c).

Further experimental data (Baker et al., 1970, 1980) in an isothermal batch reactor are related to a slight addition of fuels to slowly reacting H_2/O_2 mixtures. Using other primary free-radical sources, these data (containing a large amount of intermediate species) allow a reliable study of propagation reactions.

Transient Behavior of Jet-Stirred Flow Reactor

Thermochemical oscillations and the NTC behavior of *n*-heptane and isooctane have been extensively studied in a JSFR (D'Anna et al., 1992; Cavaliere et al., 1993; Ciajolo et al., 1993; Kurz et al., 1995) operating at high pressures. Temperature measurements inside the reactor were made by a coated Pt-Pt/Rh 13% fine-wire thermocouple with fast-response characteristics (1 ms) in order to follow the thermal oscillations that characterize the dynamic behavior of low-temperature oxidation. Hydrocarbons and oxygenated hydrocarbons were analyzed by GC/FID. GC/MS analysis allowed the detection of even trace amounts of intermediate species that are indicators of the different chemical paths.

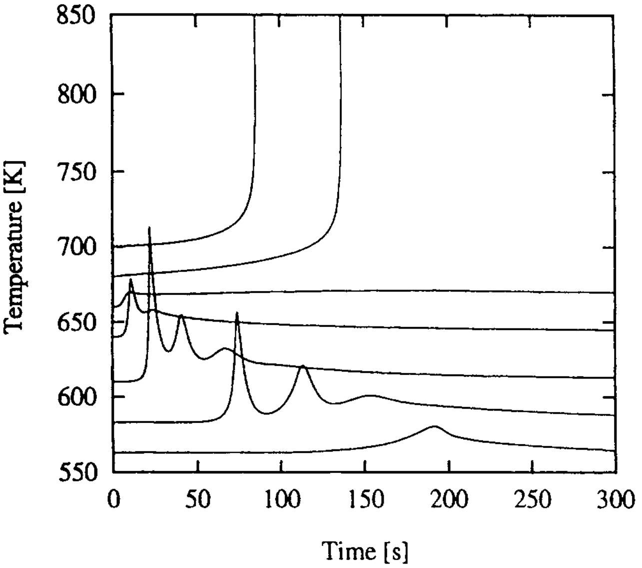

Figure 8. Calculated temperature–time profiles for the oxidation of propane/air mixtures ($\Phi = 4$) at 600 torr in a static reactor; effect of initial temperature.

Few comparisons with *n*-heptane and isooctane oxidation are presented, and the main features are discussed in order to analyze in a unified way the general aspects to the low-temperature oxidation of these large hydrocarbons. Predictions were obtained by considering an ideal, jet-stirred flow reactor, neglecting any heterogeneous reactions, and assuming the value of the internal heat-transfer coefficient suggested by Lignola et al. (1988). As already discussed (Ranzi et al., 1995c), the system is not very sensitive to the heat-transfer coefficient.

The behavior of the temperature–time profiles is similar to the one already shown for static reactors (Figure 8). As the inlet temperature is raised, the system moves from slow combustion to oscillating cool flames sustained by the continuous feed. The frequency of these cool flames increases with the temperature. Moreover, the oscillation amplitudes, both in the reactor temperature and fuel conversion, are higher at reduced conditions, that is, lower temperatures, pressures, and/or short contact time.

The predicted behavior reproduces the experimental observations in more than just a qualitative way (Ranzi et al., 1996), thereby supporting the kinetic parameter selections. At temperatures higher than 635 K, experiments and model predictions indicate damped oscillations, and a steady-state solution is reached in a few seconds.

Sensitivity analysis on the primary propagation reactions shows that the frequency (as well as the reactivity of the system) is mainly affected by the decomposition reaction of ketohydroperoxides. Figure 9 contains the comparison of the ignition diagram of a stoichiometric isooctane/air mixture at a fixed residence time of 0.4 s in the JSFR. The ignition curves delimit regions where different dynamic behaviors arise (slow combustion, cool flames, high-temperature ignition). At pressures lower than 3 bar, isooctane does not exhibit reactivity up to 900 K. A typical slow combustion regime is shown in the 500–570 K temperature range, while cool flames occur in

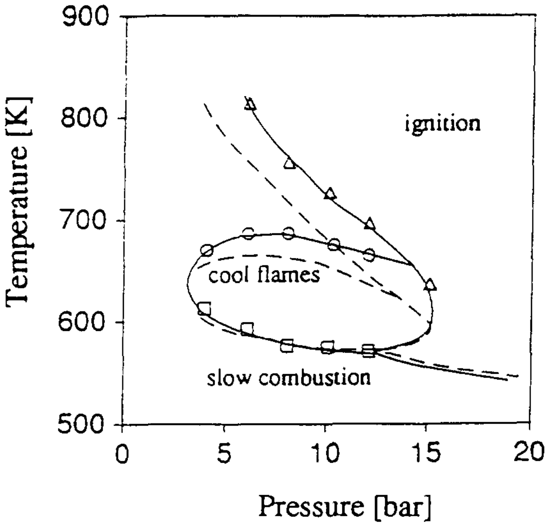

Figure 9. Ignition diagram of stoichiometric isooctane air mixtures in a JSFR at 0.4-s residence time.

Comparison between model predictions (----) and experimental measurements (□, △, ○).

the closed region of parameter space from 3 up to 15 bar and up to 670 K. A further increase in the temperatures causes a progressive reduction of the heat release rate, which characterizes the NTC region. At the end of the NTC region, hot ignition occurs and fuel conversion steeply increases. Of course these explosion diagrams are dependent on residence time.

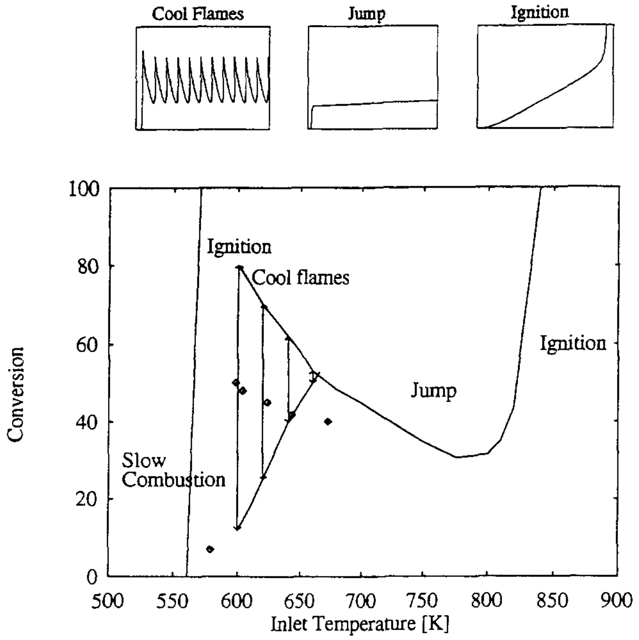

Figure 10. Oxidation of a stoichiometric n-heptane/air mixture in a JSFR at 2 bar and 0.2-s residence time.

Comparison between model predictions (——) and measured (◇) fuel conversions vs. inlet temperature. Arrows represent the predicted cool-flame oscillations. Experimental data in the oscillating cool-flame region represent the average value of conversion. Typical calculated conversion profiles are reported in the small boxes.

Also n-heptane presents the complete variety of these dynamic behaviors and shows the same structure of the ignition diagram. Due to its higher reactivity, a shift toward lower pressures is observed at shorter residence times. At 2 bar and 0.2 s, n-heptane also exhibits the different regions of slow combustion, oscillating cooling flames, negative temperature coefficient, and ignition. These phenomena are presented in Figure 10 in terms of fuel conversion as a function of the inlet temperature. Experimental data in the oscillating cool-flame region represent the average value of conversion. Conversion of the fuel is very low below 560 K, and by slightly increasing the temperature, hot ignition is predicted up to 610 K where cool flames first appear. A further temperature increase leads first to the NTC and then to the hot-ignition regions. These different conversion profiles are reported in the small boxes of Figure 10.

This set of experimental data also contains detailed information on the yields of several oxygenated intermediates at low conversion, which is useful in confirming the reference kinetic parameters of the different classes of reaction.

Conclusions

A general kinetic scheme for hydrocarbon oxidation, both in the low- and high-temperature ranges, has been developed based on very few intrinsic kinetic parameters.

All of the complex behaviors observed in different experimental systems can be explained on the basis of the same

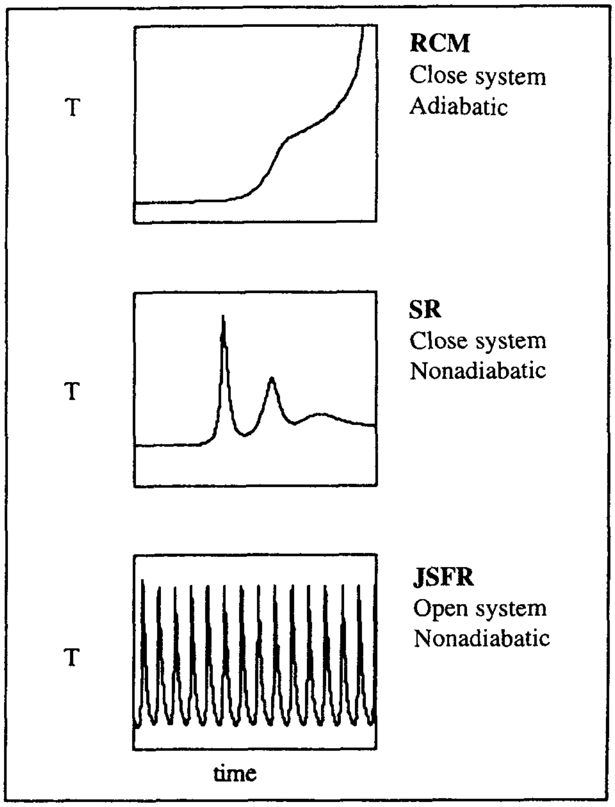

Figure 11. Calculated temperature profiles in different experimental devices.

Cool flames originated by ketohydroperoxides decomposition are observed in different ways depending on heat and mass-flow conditions.

critical reaction steps. For example, cool flames are originated by the ketohydroperoxide decomposition and can be observed in different ways, depending on the experimental device, as shown in Figure 11. The sudden temperature increase reduces the relative importance of the low-temperature mechanism and the global reactivity. If the system is assumed adiabatic, as in the RCM experiments, the temperature is kept constant through a second induction period that leads to high-temperature ignition. In nonadiabatic static reactors the heat flow reduces the system to low temperatures where again it is possible to have successive dumped cool flames. Finally, for JSFR systems, oscillatory cool flames are detected and well reproduced by the model.

This scheme models the overall set of experimental data from various reactors with vastly different operating conditions in terms of temperatures, pressures, residence times, and stoichiometries. The model (available upon request) and reported elsewhere (Gaffuri, 1995; Gaffuri et al., 1996), consistently matches the observed NTC behavior of pure alkanes from propane to isooctane. This work enhances the ability of chemical kinetic models to predict the global reaction features, such as fuel consumption and heat release, over a range of conditions for alkanes. It also suggests a technique that will be successful for the extension of kinetic models to larger hydrocarbons. In order to achieve a better knowledge of more detailed reaction features, fuller characterization of the oxidation of intermediate species such as alkenes and oxygenates and of other hydrocarbon classes is required. Oxygen addition and radical addition to double bond also requires more experimental and modeling work.

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