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A short mechanism for the low-temperature ignition of n-heptane at high pressures

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HIGHLIGHTS

- The San Diego mechanism is enhanced to obtain low-temperature ignition of n-heptane.
- We added few elementary steps and rate parameters from chemical-kinetic literature.
- The chemical mechanism capture both the NTC phenomena and the two-stage ignition.
- The short mechanism produces agreement with experimental ignition-time data.

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ABSTRACT

The low-temperature ignition of mixtures of n-heptane and air at elevated pressures (13–40 bar) is addressed. A base mechanism of 272 elementary reactions among 45 species, which models the ignition time of this fuel under a wide range of conditions for initial temperatures above about 1000 K is revised and augmented to produce the two-stage ignition and negative-temperature-coefficient (NTC) behavior seen experimentally for this fuel below 1000 K. By using available kinetic data, it is shown that by adding only 4 additional species to the original chemical mechanism, removing 8 of the original steps and replacing them by 14 new steps, the low-temperature ignition phenomena are modeled well. The numerical ignition-time predictions of this mechanism are compared with results of experimental shock-tube measurements in which NTC behavior and two-stage ignition are observed, showing reasonably good agreement. These results thus extend the range of applicability of the original mechanism to lower temperatures that are of interest in various applications, such as those for HCCI engines.

1. Introduction

The auto-ignition of heavy hydrocarbon–air mixtures has been the subject of numerous experimental and theoretical investigations [1–14]. The thermal auto-ignition delay time is one of the most important parameters in many combustion applications. This time reflects the influences of the controlling chemical process in compression-ignition engines, and it plays a role in low-temperature, high-pressure reactive-shock and detonation phenomena, as well as in many situations involving safety concerns. Investigations of auto-ignition for hydrocarbon–air mixtures indicate a two-stage ignition process involving first low-temperature then high-temperature chemical kinetics. Therefore, both types of chemical rate parameters are needed for calculation of ignition histories. A number of different sources for these rate parameters are now available in the literature [2–10]. For heavy hydrocarbons, the number of elementary steps in the tabulations ranges from the low hundreds to the high thousands, and hundreds of species have been considered. Two extreme views that can be adopted for tabulating mechanisms for any given fuel are to try to be as all-inclusive as possible, retaining every known step, or to attempt to construct mechanisms that are as short as possible, keeping only those steps that significantly affect the combustion processes of interest. Both views are justifiable, the first clearly being applicable over a wider range of conditions and being capable of describing many more aspects of the chemistry, but the second is quicker and easier to use, given current limitations on computational resources.

The San Diego mechanism (http://combustion.ucsd.edu) falls into the latter category. It is complete through the C_3 alkane propane. For many applications, however, this is sufficient, and for propane, excluding NO_X processes, it contains only 235 elementary steps [14]. It also contains a sub-mechanism for n-heptane [15,16], involving an additional 37 reactions, which models the

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oxidation of this fuel at high temperature. Offsetting this advantage of relatively few reactions is the disadvantage that it is not applicable to low-temperature auto-ignition of n-heptane, especially important for automotive applications. This disadvantage has been brought out quite clearly in a recent combustion-modeling study [17]. The purpose of the present communication is to remove this deficiency by including the relevant lower-temperature chemistry to produce the two-stage ignition and negative-temperature-coefficient (NTC) behavior seen experimentally for this fuel below 1000 K. To achieve this objective consistently within the philosophy of the mechanism, rather than including all of the potentially relevant high-temperature and low-temperature auto-ignition steps prior to the reduction and then proceeding to make the reduction from considerations of all of these steps, as has been done earlier [9], only those steps that significantly influence the ignition history over the specified range of conditions of interest are retained here.

It is worth pointing out that there are many earlier reduced-chemistry descriptions that address low-temperature chemistry and NTC ignition, such as the work reported in [18–20]. These range from empirical descriptions [18] to approaches designed to capture more than just ignition times, as may be seen from an earlier review [20]. The present contribution differs from them in that it is designed to be used in conjunction with a particular existing mechanism, to extend the applicability of that mechanism. It is not designed to stand alone or to work with other mechanisms.

It is also worth pointing out that many aspects of the low-temperature chemistry cannot be addressed on the basis of the present mechanism. For example, there are many different paths in the low-temperature chemistry, even for the smaller alkanes [21], and to achieve the maximum degree of reduction possible for addressing autoignition, their paths are excluded. Thus, for example, it is not possible to treat the formation of cyclic ethers [22,23] with the present mechanism. The objective here, thus, is a limited one, and larger mechanisms are needed to encompass these additional processes.

2. The negative-temperature-coefficient behavior

A unique phenomenon occurs during auto-ignition at temperatures below about 1000 K. Usually, as the temperature is raised, the ignition delay time of any fuel–oxidizer mixture decreases. For many hydrocarbon fuels, however, at a certain (typically low) temperature, this dependence is reversed, and the ignition delay becomes longer as the temperature is increased. Then, at a higher temperature, generally about 50–100 K higher, the ignition delay begins to decrease again, resuming its normal behavior. This phenomenon is called negative-temperature-coefficient (NTC) behavior, the temperature range over which the normal dependence is reversed being termed the NTC zone, which divides a region of low-temperature kinetics from a region of high-temperature kinetics.

For a general description of this phenomenon by the approach to be adopted here, a detailed explanation can be found in a recent publication [14]. If R denotes the alkyl radical, I the intermediate radical produced by the first addition of an oxygen molecule to R, and J the radical resulting from the further addition of now a second oxygen molecule to I, i.e. $R + O_2 \leftrightarrow I$ and $I + O_2 \leftrightarrow J$, then a generic description of the chemistry for any normal alkane can be described in a shorthand notation. Actually two types of isomers result from the first O_2 addition, and they are traditionally denoted by RO_2 and QOOH (hydroperoxyalkyl radical), respectively, but I includes both of these because it is not necessary to distinguish between them in the general description. More specifically, RO_2 achieves a steady state and so does not appear explicitly, although it is important in producing HO_2 along with the conjugate alkene, and so that important step is ascribed to the QOOH, which is retained. The symbol J stands for the hydroperoxyalkyl peroxy radical commonly denoted by O_2QOOH. Unlike I, the intermediate J is sufficiently active that it always obeys a good steady-state approximation. Besides dissociating back to I and O_2, J also decomposes to a third intermediate K (the carbonylhydroperoxide that has been denoted by OQOOH in some papers and by KET in others, it being a keothydroperoxide), $J \rightarrow K + OH$, interestingly enough at a rate that is slower than its rate of re-dissociation at the prevailing temperatures but which has an activation energy less than its heat of dissociation.

The result of these peculiar temperature dependences is that, with increasing temperature, proportionally more of the J removal occurs by dissociation, rather than by decomposition. The third intermediate K, the carbonyl compound, unlike the other two intermediates, decomposes to radicals in a strongly chain-branching process, $K \rightarrow PRODUCTS + OH$. This last chain-branching decomposition chemistry occurs at an overall rate that is substantial, but with an overall activation energy that is significantly greater than either of the two heats of dissociation of the isomers I and J. At sufficiently low temperatures, the backward dissociation step for I is negligible because of its high activation energy, and the chemistry goes sequentially from R to I through the steady-state J to K, the decomposition of which finally produces branching. As the temperature is increased, therefore, causing the rates and hence the overall concentration levels to increase, the first modification to the low-temperature sequence is the development of the K steady state. This causes the branching rate through K to become controlled by the K production rate from J. Since J is in steady state and its production rate has no explicit temperature dependence, while its consumption rate is dominated by its re-dissociation with significant activation energy, the J concentration decreases rapidly with increasing temperature in this regime. This decrease is rapid enough that, since the activation energy for J dissociation exceeds that for its decomposition to K, the production rate of K decreases with increasing temperature. The decreasing concentration of J with increasing temperature during the K steady state thus is the immediate cause of the NTC onset.

The phenomenon of two-stage ignition goes hand-in-hand with this NTC behavior. In this phenomenon, the product concentration, or temperature, for example, increases at a rate that at first accelerates with time during the first stage, then slows dramatically, remaining at a rate near zero for a period of time, before accelerating again during the second stage. This behavior also is readily understood on the basis of the simplified model given above. It occurs in the NTC zone. For any given initial temperature in this zone, at the beginning of the ignition process, the concentration of the intermediate K is zero, and so the history proceeds just as it would in the low-temperature region, with the K concentration increasing, appearing as though acceleration to an ignited state would smoothly occur. But then the K concentration reaches its steady-state value, and the subsequent rapid decrease in the concentration of J with increasing temperature decreases the branching rate, causing the onset of the second stage. This much slower overall rate then persists (through the temperature at which I production achieves partial equilibrium), until the high-temperature branching accelerates the rate of fuel consumption and R production. In view of this two-stage behavior, the relevant overall ignition delay time is that of the second stage, measured from the beginning of the first-stage process.

At lower temperatures in the NTC region, as the low-temperature region is approached, the second stage becomes very short compared with the first stage and involves only small concentration changes, and it eventually disappears at low enough initial temperatures. On the other hand, at high enough initial