

Experimental study of the kinetic interactions during the low temperature pre-ignition reactions of a surrogate gasoline

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Abstract

In order to clarify possible interactions between the oxidation mechanisms of hydrocarbons in a practical fuel in the low and intermediate temperature region, several binary mixtures, as well as a surrogate fuel composed of a ternary mixture of hydrocarbons representative of the chemical families found in petrol (toluene, isooctane and 1-hexene) were studied in a Rapid Compression Machine. Ignition delay times were measured, and qualitative and quantitative analyses of the reacting mixture were performed. These results show that both 1-hexene and toluene have an influence on the reactivity of isooctane, and that cross reactions between heavy radicals such as R or RO₂ can occur in engine conditions.

Introduction

The oxidation of petrol hydrocarbons in the low and intermediate regime of temperature has been much studied in order to predict autoignition and knock in engines as well as the building up of incomplete combustion products in the low temperature regions of the combustion chambers of petrol engines. The complex phenomenology of oxidation and autoignition of selected hydrocarbons belonging to the various families of petrol hydrocarbons - paraffins, olefins, aromatics - has been extensively studied in the rapid compression machine of Lille [1-3]. It has been shown that the oxidation schemes have common paths of low-temperature oxidation belonging to the three families but also specific paths of oxidation leading to specific behaviour in the engine environment. The low temperature oxidation of alkanes is dominated by peroxidation reactions of alkyl radicals. Higher alkenes also react through the same reactions but have also specific pathways resulting from the presence of a double bond in the alkene molecule. Aromatics are much less reactive in these conditions unless they bear a long lateral alkyl chain. When hydrocarbons are mixed and react with oxygen in the complex environment typical of a petrol engine fuel, the observed differences in reactivities of the three main types of hydrocarbons may induce interactions between reaction mechanisms. In fact, octane index of binary mixtures can be higher or lower than each of the pure constituent of the mixture [4]. Before studying the surrogate fuel made of a mixture of three hydrocarbons typical representatives of the three families, it is useful to examine first the behaviour of their binary mixtures. Therefore, three binary mixtures have been studied: isooctane/toluene 65/35, isooctane/1-hexene 82/18, toluene/1-hexene 70/30, and finally a surrogate fuel composed of 47 %

isooctane, 35 % toluene, and 18 % 1-hexene. Compositions are given in mole fractions.

Experimental

These hydrocarbon mixtures were mixed with stoichiometric quantities of oxygen diluted as air in various mixtures of carbon dioxide/nitrogen/argon in order to modify the heat capacity. They can then reach temperatures from 600 to 900 K by rapid compression in our experimental apparatus, which has been described widely in previous papers [1]. The mixture is compressed in 60 ms, and the volume is kept constant in the end of the compression as the pressure and light emission profiles are recorded. The reaction volume is a cylinder of volume 40 cm³, and the compression ratio is $\rho = 9.5$. The autoignition delay times, and, if occurring the cool flame delay times, are deduced from the light emission and pressure traces. The temperature at the end of compression T_C was calculated using an adiabatic core gas model [1]. Detailed qualitative and quantitative were performed after quenching the reaction by allowing an adiabatic expansion of the mixture at a selected time after the compression. The residence time of the mixture is determined by inspection of the pressure profile. The samples are characterised by gas chromatography techniques, coupled with mass spectrometry and FID-TCD detectors. Compositions of the gas mixtures are given in selectivities i.e. in number of carbon atoms of each analysed species for 100 initial carbon atoms.

Results and Discussion

The phenomenologies of autoignition by rapid compression of the three binary mixtures and the surrogate fuel have been recognised by measuring mono- or multistage autoignition delay times at different temperatures and pressures at top dead center

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and comparing them to similar measurements made on pure hydrocarbon/"air" mixtures. As the overall reactivity depends strongly upon the initial partial pressures of hydrocarbons and oxygen, which vary according to the mixtures, a direct comparison of ignition delay times is not easy to interpret. Results are easier to interpret by comparing Arrhenius plots. The temperature coefficients of the rates, which are supposed to be much less dependent on the partial pressures, can be directly compared and used as a better characteristic of the reactivity of the hydrocarbon mixtures. It has been observed that in the case of temperatures over 1000 K, the interactions between hydrocarbons oxidation take place through a common radical pool of small radicals like H, O, OH, HO₂ and CH₃. [5]. As a consequence it has been possible to build high temperature kinetic mechanisms for mixtures by adding the two mechanisms of oxidation for the pure hydrocarbons [6]. The accurate modelling of the behaviour of mixtures in the low and intermediate temperature region might not be so easy, as in the low temperature range parts of the initial structure of hydrocarbons are kept and complex interactions between heavier radicals like R and RO₂ may occur. Detailed analyses of the reaction mixtures during the autoignition delays have been performed in order to identify mixed intermediate products resulting from possible interactions between the mechanisms of oxidation of the hydrocarbon partners through cross reactions.

Isooctane/toluene 65/35 mixture

Pure toluene does not exhibit any low temperature reactivity. It can only be ignited by compression above 910 K at 17.5 bar after a delay time longer than 200 ms. There is no cool flame and the rate transition at autoignition is very sharp. By contrast, pure isooctane shows a two-stage autoignition between 650 and 800 K and a well marked negative temperature coefficient between 700 and 800 K. As seen in figure 1, addition of toluene increases the temperature coefficients of the cool flame and of the total delay times when autoignition occurs in two stages. This can be the result of an inhibiting effect of the easily formed stabilised benzyl radical. As a result, the negative temperature coefficient of the mixture is less marked. One can also notice that the cool flame range exhibited by pure isooctane is reduced by the presence of toluene.

At higher temperature, when ignition takes place in one stage, the inhibiting effect of toluene is much less significant, unless the amount of toluene reaches 70 % of the mixture (Figure 2). Analysis of the reaction mixture during the pressure "plateau" that follows the first stage of autoignition shows that both of the hydrocarbons react during the cool flame event and are converted up to 30 % for isooctane and 25% for toluene (Figure 3).

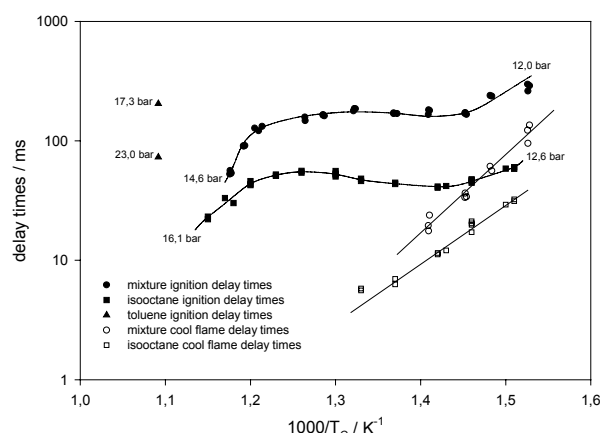


Fig. 1: Arrhenius plot of the ignition delay times of isooctane, toluene and their 65/35 mixture and cool flame delay times of isooctane and the mixture.

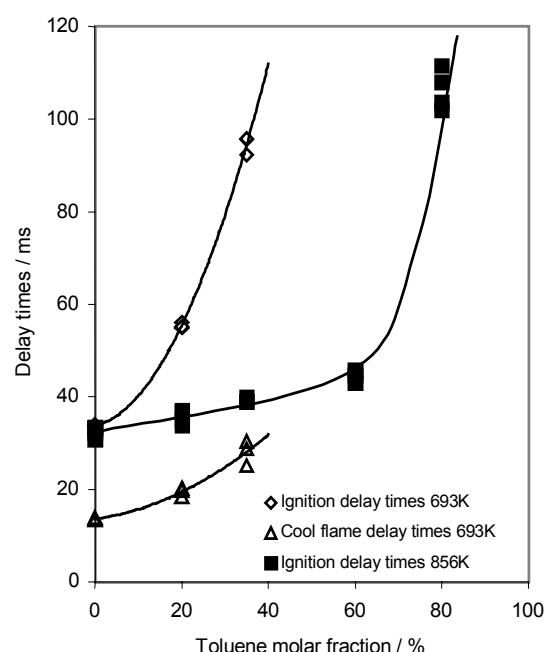
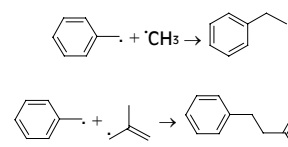


Figure 2: Ignition and cool flame delay times of isooctane/toluene mixtures versus toluene mole fraction.

Isooctane being more reactive generates a pool of small radicals, mainly HO₂ and OH, responsible for the conversion of toluene at the relatively low temperature of the cool flame. Carbon monoxide rises progressively from the cool flame event to a maximum of 0.2 % at the onset of the final ignition. In addition to the oxidation products of pure isooctane and pure toluene, two products resulting from cross reactions between stable radicals are formed: ethylbenzene and (3-methyl-3-butenyl)benzene. The formation of these products can be explained by the following reactions:



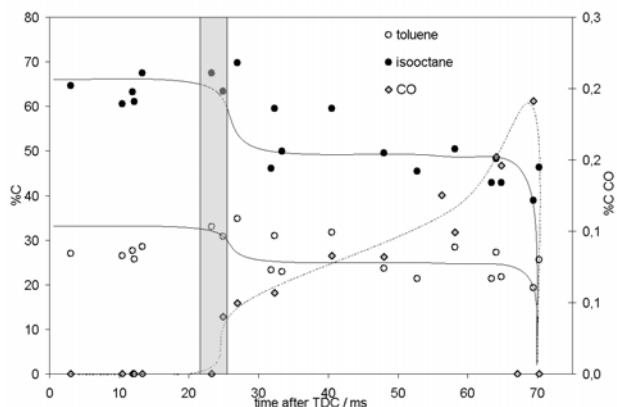


Figure 3: Concentration profiles of initial hydrocarbons and carbon monoxide after rapid compression of an isooctane/toluene 65/35 mixture. The cool flame is figured by the gray rectangle. $T_C = 700$ K.

Isooctane/1-hexene 82/18 mixture

Pure 1-hexene shows a two-stage autoignition between 660 and 800 K with a weakly negative temperature coefficient between 750 and 830 K. 1-Hexene does not change significantly the phenomenology of autoignition of isooctane (Figure 4). Ignition delays are reduced by 1-hexene in the whole range of temperature studied.

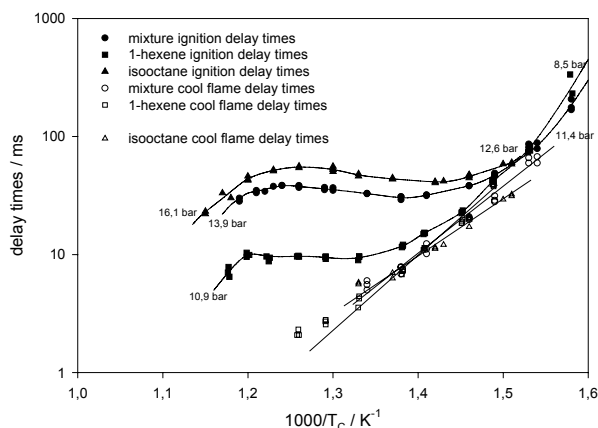


Fig. 4: Arrhenius plot of the ignition and cool flame delay times of isooctane, 1-hexene and their 82/18 mixture.

No products of cross reactions have been detected. The analyses performed show that each of the initial hydrocarbons react during the cool flame up to 25 % for isooctane and 30 % for 1-hexene. The building up of carbon monoxide starts at the cool flame and reaches a maximum of 0.25 % at the onset of the final ignition. Oxidation products from both of the two components of the mixture were detected.

Toluene/1-hexene mixture

Differences in the temperature coefficients are very slight below 690 K. Above 690 K, the addition of toluene results in a clear increase of the temperature coefficient until 810 K. In the higher temperatures, the temperature coefficient is similar. Such an effect was

not so clear with isooctane. The cool flame delay temperature coefficient is unchanged (Figure 6).

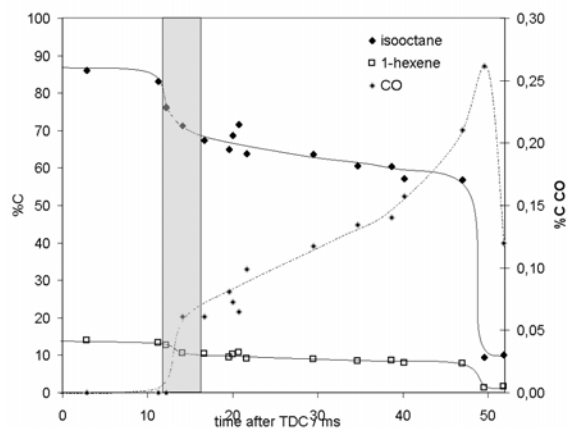


Figure 5: Concentration profiles of initial hydrocarbons and carbon monoxide after rapid compression of an isooctane/1-hexene 82/18 mixture. The cool flame is figured by the gray rectangle. $T_C = 702$ K.

Analyses of the reaction mixtures show that both hydrocarbons are converted during the cool flame event up to 15 % for toluene and 30 % for 1-hexene. Carbon monoxide starts to build up during the cool flame and increases progressively until the final ignition when it reaches 0.23 % (Figure 7).

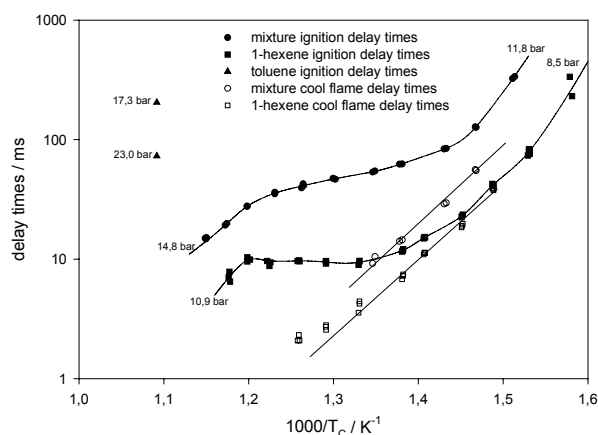


Fig. 6: Arrhenius plot of the ignition delay times of toluene, 1-hexene and their 70/30 mixture and cool flame delay times of 1-hexene and the mixture.

During the pressure "plateau" that follows the first stage of reaction, a relatively high amount of various aromatic products is formed. This shows for the first time that toluene can develop reaction channels although the temperature is rather low (about 700 K). As in the isooctane/toluene mixture, toluene is cooxidised by the pool of small radicals generated by the relatively more reactive 1-hexene. Cross reactions between stable radicals gives ethylbenzene, styrene, butenylbenzene, 3-phenylpropanal, 4-phenylbutanone, (3-heptenyl)benzene. Dibenzyle is also formed, although it has not been detected in the case of other

mixtures containing toluene. The formation of these cross products results from the recombination of the benzyl radical with long-living radicals coming from the oxidation of 1-hexene [2], like an allylic hexenyl radical to give (3-heptenyl)benzene, the allyl radical to give butenylbenzene, or with another benzyl radical to give dibenzyle.

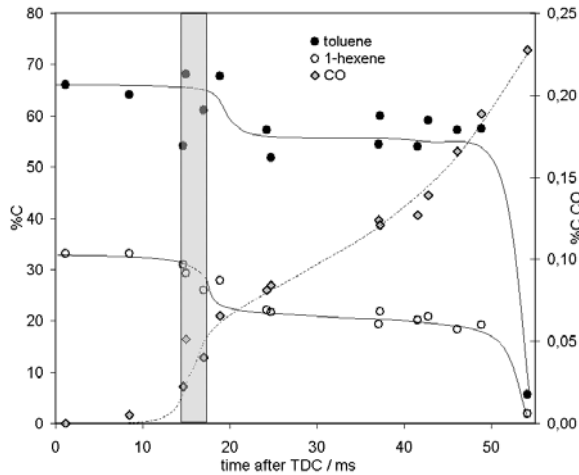


Figure 7: Concentration profiles of initial hydrocarbons and carbon monoxide after rapid compression of a toluene/1-hexene 70/30 mixture. The cool flame is figured by the gray rectangle. $T_C = 709$ K.

Surrogate fuel

The surrogate fuel shows a two-stage autoignition between 650 and 750 K and a slightly negative temperature coefficient between 740 and 780 K. Its phenomenology differs from isooctane but looks like that of hexene, even though there is 2.6 times more isooctane. The temperature coefficients of the cool flame delays and the final ignition delays are quite similar to the ones of 1-hexene, except that the negative temperature coefficient region is shifted towards lower temperatures (Figure 8).

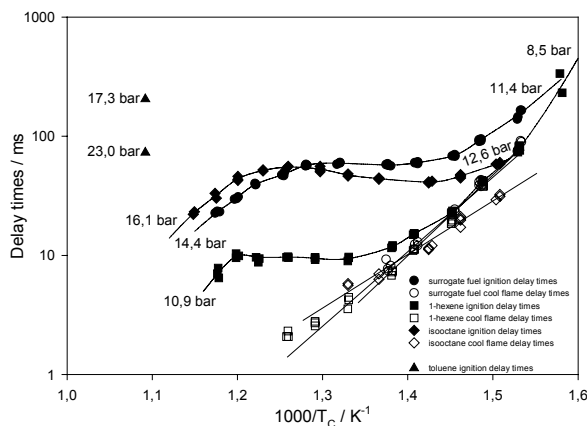


Fig. 8: Arrhenius plot of the ignition delay times of toluene, 1-hexene, iso-octane and the surrogate fuel and cool flame delay times of 1-hexene, iso-octane and the surrogate fuel.

This could bear some relation to the high blending research octane number of 1-hexene (96) compared to the pure research octane number (76.4) and to the well-known octane bonus of olefins in the blending manufacture of petrol. All of the initial hydrocarbons react during the cool flame. Isooctane and 1-hexene form the typical low-temperature oxidation products previously found, and toluene forms some of the products detected in the case of the toluene/1-hexene mixture. Cross reaction products are the same as in the binary mixtures, but are formed in lower quantities. Dibenzyle is also found as a trace product.

The comparison of the behaviours of 1-hexene, the toluene/1-hexene 70/30 mixture and the surrogate fuel (Figure 9) shows that the phenomenology of the surrogate fuel is nearly identical to the phenomenology of the toluene/1-hexene mixture for temperatures above 700 K. The temperature coefficient for the cool flame delay times is the same for 1-hexene alone, the 1-hexene/toluene mixture and the surrogate fuel.

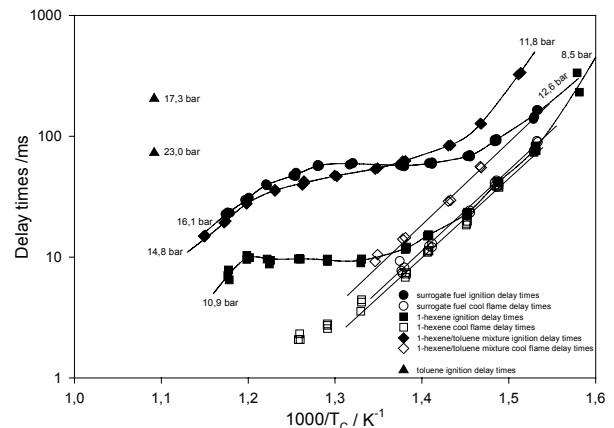


Fig. 9: Arrhenius plot of the ignition delay times of toluene, 1-hexene, the toluene/1-hexene 70/30 mixture and the surrogate fuel and cool flame delay times of 1-hexene, the toluene/1-hexene 70/30 mixture and the surrogate fuel.

Further comparison of the temperature coefficients of the different hydrocarbons and mixtures (Figure 10) allows to draw some more conclusions about the blending effects of the hydrocarbons present in the surrogate fuel :

- The addition of 1-hexene to isooctane reduces slightly the extent of the negative temperature coefficient region and the coefficient itself. The transition region from the intermediate to the low temperature regime is broadened.
- The addition of toluene to iso-octane reduces more the extent of the negative coefficient region and the coefficient itself. The transition from the intermediate to the high temperature regime is broadened.
- For the surrogate fuel, the extent of the negative temperature coefficient region is intermediate, but the coefficient itself is the smallest. Both transitions regions from the intermediate regime are broadened.

- 1-Hexene has the strongest impact on the temperature coefficient of the low temperature regime, and toluene on the high temperature regime.

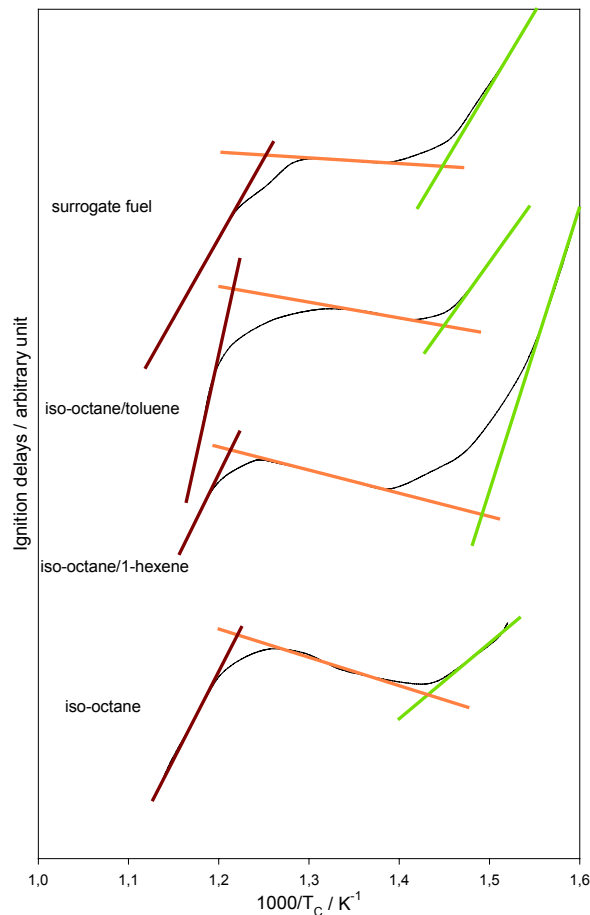


Fig. 10: Arrhenius plot of the ignition delay times of iso-octane and some of the mixtures.

Conclusion

The comparison of the phenomenology of autoignition of iso-octane, 1-hexene, toluene and their mixtures shows that 1-hexene modifies mainly the low temperature regime whereas toluene modifies mainly the high temperature regime of iso-octane. 1-Hexene may have an influence on the balance between HO_2 and OH radicals generated by iso-octane as both can add to the double bond. Toluene forms easily benzyl radicals which can add HO_2 , forming new intermediate temperature branching agents. When both are blended with iso-octane, they undergo cross reactions leading to new termination steps.

Acknowledgements

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