



## Nitric oxide interactions with hydrocarbon oxidation in a jet-stirred reactor at 10 atm

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Received 4 February 2005; received in revised form 16 November 2005; accepted 6 January 2006

Available online 23 February 2006

### Abstract

The purpose of the present work is to better define the influence of trace amounts of NO on the oxidation of model fuels such as *n*-heptane, iso-octane, toluene, and methanol. This information is of interest for understanding and modeling autoignition whether for engine knock or for engines operating under compression ignition modes such as HCCI (homogeneous charge compression ignition) or CAI<sup>TM</sup> (controlled autoignition). The experiments were performed in a jet-stirred reactor at 10 atm over a temperature range of 550 to 1180 K with a residence time of 1 s for stoichiometric mixtures highly diluted in nitrogen. The carbon content was about 1 molar percent and the added NO ranged from 25 to 500 ppmv. The effects of NO vary with the temperature regime. At the lowest temperatures NO inhibits the reaction. As temperature rises beyond 675 K, NO can considerably accelerate the reactivity of all fuels to an extent that can supercede the NTC behavior in the case of *n*-heptane. Modeling work indicates that in this temperature region at 10 atm the promoting effect of NO is largely due to the catalyzed production of OH, involving the dissociation of HONO, with the latter formed from reactions between NO<sub>2</sub> and HO<sub>2</sub>, CH<sub>3</sub>O, or CH<sub>2</sub>O. In the intermediate temperature regime the intensity of the accelerating effects is observed to rise with the octane number of the fuel, with the exception of methanol. For toluene, the onset of oxidation drops down from 900 to 800 K with as little as 50 ppmv NO.

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**Keywords:** Hydrocarbon oxidation; NO<sub>x</sub> sensitization; Kinetic modeling

### 1. Introduction

The effect of residual burnt-gas composition on combustion characteristics is of interest owing to the increasing use of EGR (exhaust gas recirculation) in various types of piston engines. In standard spark

ignition engines the problem pertains to the occurrence of engine knock, which is a deterrent to engine efficiency. In diesel engines there may be some effects on ignition delay, although most of the timing is determined by the point of fuel injection. The present interest focuses more on new configurations of engines under development that use homogeneous charge compression ignition (HCCI) over some range of engine operating conditions. The advantages are

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reduced  $\text{NO}_x$  and HC emissions and improved combustion stability and overall engine efficiency. In four-stroke spark-ignition engines the fuels are resilient to ignition and considerable quantities of uncooled EGR (exhaust gas recirculation) are needed to activate and control the onset of combustion as in the CAI<sup>TM</sup> system [1,2]. In diesel engines the fuels used are easily ignited and large amounts of cooled EGR are needed to retard and attenuate the onset and the rate of combustion [3,4]. The implementation of compression ignition modes in engines requires sound control strategies for ignition timing, which can benefit from better understanding and modeling of the interactions of hydrocarbon chemistry with the various burnt-gas constituents, of which NO is one.

Trace amounts of NO are known to alter hydrocarbon combustion and is potentially the most active of the residual burnt-gas constituents [5]. This molecule has been shown to have accelerating or inhibiting characteristics on the oxidation of *n*-butane [6,7], 1-pentene [8], methanol [9–11], ethane [12], propane [13], DME (dimethyl ether) [14, 15], methane [16,17], and ethylene and ethane [18], depending on the temperature–pressure regime and on the amount of NO. For the most part, these studies were performed in various configurations of plug flow reactors where back-mixing is not important. Studies have also been performed with an 87 octane number *n*-heptane/iso-octane blend and with a similar full-blend gasoline [19] at 12.5 atm. Nitric oxide substantially changes the low- and intermediate-temperature combustion rates of this blend. Below the turnover temperature at 12.5 atm (~620 K), very small concentrations of nitric oxide (<5 ppmv) accelerate the reaction, whereas larger quantities (50 ppmv) inhibit it. To our knowledge, no studies have been performed on the interactions of NO with the pure reference fuels *n*-heptane and iso-octane.

The effect of NO on ignition characteristics has been investigated in single-cylinder research engines [3,20–22] and in a nonpremixed laminar counterflow configuration [23]. The first study observed ignition to start slightly earlier in the presence of NO and the second showed hydrocarbon ignition temperatures to drop when NO was added to the oxidizer stream. Experimental reports on ignition delay times from shock tubes or in rapid compression machines are currently lacking.

The present study aims at better defining the interactions of NO with the oxidation of *n*-heptane, iso-octane, methanol, and toluene. These hydrocarbons are chosen to represent various fuel families of specific ignition and combustion characteristics in engines. The experiments are performed in a jet-stirred reactor at 10 atm and over a temperature range of 550 to 1180 K. In this configuration the tempera-

tures, pressures, and aerodynamic back-mixing approach engine conditions at ignition. The data provide a means of comparing the strength of the effects among the four hydrocarbons and constitute a database for developing and testing detailed kinetic models of this chemistry.

## 2. Experimental

The experimental setup used has been presented in detail elsewhere [24] and is described only briefly. The jet-stirred reactor (JSR) is a 4-cm-diameter fused-silica sphere. It is equipped with four 1-mm inside diameter nozzles that inject the gases at high velocity to generate intense turbulence and homogenize the mixture. Nitrogen, oxygen, and NO are measured and regulated by mass flow controllers. The liquid fuels are delivered by a high-pressure liquid chromatography pump into a vaporizing system. To atomize the liquid fuel and prevent reactions prior to entering the reactor, a secondary stream of nitrogen carries the fuel through a capillary, up to the final mixing point, located just prior to the reactor entrance. The arrangement of the nozzles makes it possible to move an uncooled gas sampling quartz microprobe as well as a thermocouple along the vertical axis of the reactor. The thermocouple (Pt/Pt-Rh 10%) is contained inside a quartz envelope to avoid potential catalytic effects.

Samples of the reacting mixtures are drawn continuously through a heated Teflon line to a Fourier transform infrared spectrometer (FTIR); the optical cell is heated to 120 °C at 500 mbar to prevent condensation of water. Discrete samples are also collected in 1 litre Pyrex bottles at 30 to 50 Torr for later gas chromatographic (GC) analysis. The chromatograph is equipped with two 0.53-mm i.d. capillary columns, one a Poraplot, and the other a 5-Å molecular sieve. The columns are coupled to a thermal conductivity detector (TCD) that is followed by a flame ionization detector (FID). Experimental mole fraction measurements were obtained for the injected reactants  $\text{CH}_4$ , ethane, ethylene, acetylene, propene, iso-butene, 1-pentene, 1-hexene, and benzene, using chromatographic techniques with uncertainties of  $\pm 10\%$  except for toluene and benzene, where the uncertainties reach  $\pm 15\%$ . Measurements of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_2\text{O}$ , NO, and  $\text{NO}_2$  were made using the FTIR spectrometer with uncertainties of  $\pm 10\%$ . Only those species that best portray the effects of NO are shown in Section 3.

A series of experiments with stoichiometric mixtures of *n*-heptane, iso-octane, toluene, and methanol were carried out at a mean residence time of 1 s at 10 atm. The temperature was varied from 550

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