Combustion and Flame 156 (2009) 348–361

Contents lists available at ScienceDirect

Combustion and Flame

www.elsevier.com/locate/combustflame

Chemiluminescence of BO_2 to map the creation of thermal NO in flames

D. Maligne[a,b,c,*], A. Cessou[a], D. Stepowski[a]

[a] CORIA CNRS UMR6614, Site Universitaire du Madrillet, BP12, 76801 St Etienne du Rouvray Cedex, France
[b] Renault s.a.s., 1 allée Cornuel, 91510 Lardy, France
[c] IFP, 1 et 4 avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex, France

ARTICLE INFO

Article history:
Received 29 February 2008
Received in revised form 24 June 2008
Accepted 7 October 2008
Available online 17 November 2008

Keywords:
Nitrogen monoxide
Boron oxide
Chemiluminescence
Reaction rate

ABSTRACT

The aim of this study is to detect and map the local conditions that generate thermal NO in flames. According to the Zeldovich mechanism, the formation of NO comes from the local conjunction of a high concentration of atomic oxygen and a temperature above a critical high level imposed by the high activation energy of the rate-limiting reaction. The green light emitted when a flame is seeded with boron salts is a chemiluminescence from the BO_2^* that is chemically formed in its excited state when BO reacts with atomic oxygen. As the rate of this oxidation is also strongly increasing with temperature, the chemiluminescence of BO_2 depends on the concentration of atomic oxygen and on the temperature in a way similar to the formation rate of thermal NO. This double analogy suggests the possibility of an experimental in situ simulation of the formation rate of thermal NO or at least the use of the chemiluminescence of BO_2 to map the sites where thermal NO is being created. Spectroscopic experiments and comparisons with numerical simulations have been performed to test the feasibility of this technique in laminar premixed and diffusion methane/air flames. The agreement is good except in the burnt gases of fuel-rich flames. Imaging strategies with different spectral filters have been developed in the same flames to overcome the problem of interference from soot radiation in diffusion flames.

1. Introduction

The reduction of NO_x emissions in engines is of critical interest for industrial manufacturers. The main formation pathway of NO_x in high-temperature environments is the thermal way (Zeldovich's mechanism) [1]. For many years it has been crucial in Diesel systems due to the high temperature of the autoignited combustion ($T = 2000$ K). By using the exhaust gas recirculation technique (EGR), the combustion temperature in the Diesel engines has been decreased, and the thermal NO route does not seem to be as critical as before; however, recent work suggests that it is still the main formation pathway in Diesel engines [2]. In direct injection SI engines, thermal NO plays a major role in total NO formation. Therefore, studies of thermal NO formation are still topical and of great interest for the reduction of pollutants. This paper reports an experimental method of mapping the formation rate of thermal NO in flames.

Many experiments have been performed to measure total NO concentrations. The initial efforts were based on probe sampling techniques [3–5]. Even though they have made great progress (water-cooled probes, high dilution rates, chemiluminescence analysis), they do not provide enough spatial and time resolution to determine the formation sites of NO.

More recently, laser-based diagnostics such as the laser-induced fluorescence (LIF) of NO have provided concentration fields of NO with good time and spatial resolution, either in burner flames [6–8] or in engines [9–13]. The main problem of this technique is the noticeable absorption of the laser beam and subsequent parasitic fluorescence by oxygen, especially (and unfortunately) at high temperatures [14,15]. The fluorescence also has to be corrected for the cumulative effects of pressure, temperature, collisional quenching, and laser attenuation [9]. Finally, planar LIF may provide concentration fields of NO at the laser firing date and over the light sheet, but even if quantitative data can be derived from LIF, no information is available on the sites where NO has been created nor about its formation pathway.

Great progress has been made in numerical simulations. They provide spatial resolution of NO formation sites thanks to the modeling of the different NO formation mechanisms [16,17]. However, numerical simulations cannot yet predict accurately the location of NO formation sites in the very complex reacting flows encountered in engine chambers.

Few experimental data on NO creation sites are reported in the literature. To our knowledge, the only experimental technique for visualizing the sites where thermal NO is created was first reported by American researchers [18,19] and then investigated at Warwick University [20]. The technique is based on detection of

---

[*] Corresponding author. Current address: IFP, 1 et 4 avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex, France. Fax: +33 1 47 52 66 85.
E-mail address: david_maligne@yahoo.fr (D. Maligne).

0010-2180/$ – see front matter © 2008 The Combustion Institute. Published by Elsevier Inc. All rights reserved.
doi:10.1016/j.combustflame.2008.10.005

the chemiluminescence of a tracer, the boron dioxide BO_2^* (*: excited states). It can map the sites where NO is created, since the intensity of BO_2^* emission also increases with both the concentration of atomic oxygen and the temperature. However, the chemiluminescence imaging approach has limitations: it suffers from line-of-sight integration and above all it stays qualitative as far as the numerous involved parameters (reaction rates, quenching, concentration of parent species, etc.) are not accurately known. The purpose of the present work is to investigate this technique in detail by means of spectroscopy and imaging. Premixed and diffusion laminar methane/air flames stabilized on atmospheric-pressure burners are studied.

2. Analogy between formation of thermal NO and chemiluminescence of BO_2

2.1. Formation rate of thermal NO

The three main routes for the formation of NO are the thermal route, the prompt NO path, and the hydrocarbon route [21]. The thermal route (Zeldovich mechanism) [1] is the formation of NO via atmospheric N_2 in high-temperature environments ($T >$ 1850 K) according to the system

$$N_2 + O \xrightarrow{K_{f1}} NO + N, \tag{R1}$$

$$N + O_2 \xrightarrow{K_{f2}} NO + O, \tag{R2}$$

$$N + OH \xrightarrow{K_{f3}} NO + H, \tag{R3}$$

where the inverse reactions are neglected because of the low concentration of NO.

The formation rate for thermal NO is then given by

$$d[NO]/dt = K_{f1}[N_2][O] + K_{f2}[N][O_2] + K_{f3}[N][OH]. \tag{1}$$

The mechanism above is initiated and governed by reaction (R1), which is the slowest, especially at low temperature, since it has a high activation energy (≈320 kJ/mol). As soon as atomic nitrogen is produced by this initiation step, it is immediately consumed by (R2) and (R3) so that a quasi-steady state can be assumed for [N]:

$$d[N]/dt = K_{f1}[N_2][O] - K_{f2}[N][O_2] - K_{f3}[N][OH] = 0. \tag{2}$$

With the simplification above, expression (1) for the rate of formation of thermal NO reduces to

$$d[NO]/dt = 2K_{f1}[N_2][O], \quad \text{where } K_{f1} \propto \exp(-38{,}370/T). \tag{3}$$

Equation (3) shows that the formation of thermal NO comes from the local conjunction of high temperature and high concentration of atomic oxygen (a concentration that is difficult to measure).

2.2. Chemiluminescence of boron dioxide

The well-known green light emitted when a flame is seeded by boron salts was first identified by Kaskan et al. as chemiluminescence of boron dioxide, BO_2^* [22,23]:

$$BO + O \rightarrow BO_2, \tag{R4}$$

$$BO + O \xrightarrow{K_{f5}} BO_2^*, \tag{R5}$$

$$BO_2^* \xrightarrow{Q} BO_2, \tag{R6}$$

$$BO_2^* \xrightarrow{A_7} BO_2 + h\nu. \tag{R7}$$

In oxygen-containing environments, boron monoxide reacts with atomic oxygen to form boron dioxide, either in its ground state $X^2\Pi_g$ by (R4) or in excited state $A^2\Pi_u$ by (R5). Chemically excited BO_2^* relaxes quasi-instantaneously to its ground state either by collisional quenching at rate Q or (competitively but less probably) by spontaneous emission, called chemiluminescence, at rate A_7. The power of the chemiluminescence emitted when BO_2^* relaxes to its ground state (R7) is

$$P_{chem} = h\nu A_7[BO_2^*]. \tag{4}$$

Owing to its fast quenching, BO_2^* can be expected to be in steady state concentration according to

$$d[BO_2^*]/dt = K_{f5}[BO][O] - (Q + A)[BO_2^*] \approx 0 \quad \text{with } A_7 \ll Q. \tag{5}$$

With this approximate of $[BO_2^*]$, Eq. (4) for the power of the chemiluminescence emission reduces to

$$P_{chem} = h\nu(A_7K_{f5})/Q\,[BO][O]. \tag{6}$$

The power of the chemiluminescence emission is thus proportional to the local product of the parent species (rather than to the species itself) and in the present case it is proportional to the local concentration of atomic oxygen, which is a key factor in the formation of thermal NO (see Eq. (3)). The remark in the parenthesis above underlines a basic feature of chemiluminescence: The emitting excited species is rapidly quenched to its ground state by collisions before it can be transported out of the zone where it was created (where the action is initiated by the local conjunction of the parent species), whereas laser-induced fluorescence probes the local ground state population of an absorbing species such as it is or has been transported (convection or diffusion) from its formation place to the laser-probed point.

However, the ease of chemiluminescence experimentation (without any laser) has severe drawbacks relative to LIF: up to now P_{chem} has been carefully defined as the local power of the *emitted* chemiluminescence; actually the detected luminescence picture suffers from line-of-sight integration over the field of view of the camera, whereas in planar LIF the camera maps solely the concentration in the laser-excited field. Another drawback is the qualitative feature of chemiluminescence owing to the large uncertainty in the rate of chemical reaction K_{f5}, whereas the rate of laser pumping in LIF can be accurately monitored and/or calibrated. Nevertheless, even if qualitative, the chemiluminescence method can be helpful in detecting the sites where the parent species can meet and react, with the benefit that spatial integration over the depth of field of the camera will ensure detection of any site out of focus and the complementary drawback of lacking resolution in the third direction.

For comparison with the formation of NO, the temperature dependence of the chemiluminescence of BO_2 has been investigated using an Arrhenius form for the reaction rate K_{f5} of reaction (R5) according to

$$K_{f5} = \alpha \exp(-E_a/kT), \tag{7}$$

where the pre-exponential term α is expected to make only a negligible contribution to the temperature dependence. The activation energy E_a can also be expressed in terms of an activation temperature $T_a = E_a/k$:

$$P_{chem} = h\nu(A_7\alpha)/Q\,[BO][O]\exp(-T_a/T). \tag{8}$$

The order of magnitude of the activation energy for the reaction $BO + O \rightarrow BO_2^*$ has been deduced from the spectroscopic data acquired by Gilbert on the chemiluminescence of BO_2^* in various flames [24,25]. Among the normalized data obtained or gathered by Gilbert, we used the intensities emitted at 547 nm in three stoichiometric flames: H_2/air, H_2/O_2, C_2H_2/O_2. Once normalized by the width of the spectrometer slits and the seeding rates, the intensities I to be compared are those shown in Table 1.