1 **Quantification of HO_2 and other products of dimethyl ether oxidation**

2 **(H_2O_2, H_2O, and CH_2O) in a jet-stirred reactor at elevated temperatures by**

3 **low-pressure sampling and continuous-wave cavity ring-down spectroscopy.**

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8 **Abstract**

9 Measuring the formation of HO_2 and H_2O_2 from the oxidation of fuels is challenging but

10 extremely important for determining their tendency to follow chain-termination pathways

11 from $R + O_2$ compared to chain-branching leading to the production of OH radicals.

12 Furthermore, such data are vital for improving existing detailed chemical kinetics models.

13 Dimethyl ether (DME), a clean renewable fuel, is the simplest ether exhibiting cool flame

14 oxidation chemistry, a key-process for auto-ignition in internal combustion engines. Although

15 the oxidation of DME has been studied in the past, little information is available for the

16 production of HO_2 and H_2O_2. The oxidation of dimethyl ether was performed in a jet-stirred

17 reactor at atmospheric pressure, over a range of temperatures (~540-850 K) and equivalence

18 ratios ($\varphi = 0.5$-2) and, for the first time, the concentrations of HO_2 and H_2O_2 were measured

19 using a newly developed experimental setup involving low-pressure sampling and near-

20 infrared cw-cavity ring down spectroscopy. Concentrations of H_2O and CH_2O were also

21 measured. These new experimental results extend the available kinetic database for the

22 oxidation of dimethyl ether which is needed to assess the validity of combustion kinetics

23 models, as shown here.

24 **Keywords** : Dimethyl ether, Oxidation, Jet-stirred reactor, hydroperoxyl radical, hydrogen

25 peroxide

1. Introduction

The hydroperoxyl radical (HO_2) is an important species involved in both atmospheric[1] and combustion chemistry[2]. Via recombination, it forms H_2O_2 ($HO_2 + HO_2 \rightarrow H_2O_2 + O_2$) that is involved in the 3rd explosion limit of hydrogen[3] and is also supposed to play a key-role in homogeneous charge compression ignition[4] via its decomposition, $H_2O_2 \rightarrow OH + OH$. The hydroperoxyl radical also plays a complex role through its fast reaction with nitric oxide ($NO + HO_2 \rightarrow NO_2 + OH$) when exhaust gas recirculation is used to reduce NO_x emissions from compression ignition engines [5]. To evaluate the importance of these reactions in combustion, quantitative measurements of HO_2 are highly desirable. Moreover, they could complement recent efforts for better characterising combustion intermediates [6-9]. While such measurements [10-13] have been performed routinely at room temperature, difficulties appear at higher temperatures where HO_2 seems to be too reactive to be quantified after sampling. Recently we reported the first direct HO_2 measurements during the oxidation of n-butane in a jet-stirred reactor by using cavity ring-down spectroscopy with continuous wave light (cw-CRDS)[14]. Measurements of more stable species (H_2O_2, H_2O, and CH_2O) were also reported in that publication. Similarly to the n-butane case, the oxidation of dimethyl ether can also proceed via a cool-flame. As highlighted recently [15] the oxidation of DME has been extensively studied since the pioneer kinetic study reported in 1996[16]. Recently, measurements of HO_2 and H_2O_2 during the lean oxidation of DME in a flow-reactor have been reported[17] showing discrepancies with detailed kinetic modelling. Under their conditions, the model overestimated HO_2 by a factor of ~5 whereas H_2O_2 concentrations were under predicted by ca. 50%. Therefore, it seemed interesting to investigate further the formation of HO_2 and H_2O_2 during the oxidation of DME under well-characterized conditions. To that end, our new JSR-CRDS experimental set-up was used to study the oxidation of DME. The present data, consisting of concentration profiles of HO_2, H_2O_2, H_2O,

51 and CH_2O obtained as a function of temperature for several reacting $DME/O_2/N_2$ mixtures,

52 are presented and compared to predictions of two recent literature kinetic models.

53 **2. Experimental**

54 The experimental set-up is presented in Figure 1. It consists of (i) a Jet Stirred Reactor (JSR)-

55 sampling nozzle assembly, and (ii) a low-pressure cw-cavity ring-down spectrometer. A fused

56 silica spherical JSR with a volume of 37 cm^3 was used. The stirring is achieved by the jets

57 exiting the four 0.5 mm i.d. injectors nozzle. Details of the development and operation of such

58 reactors has been presented earlier[18]. The mean residence time of the gas mixture inside the

59 JSR can be varied from a few milliseconds to several seconds by adjusting the total inlet gas

60 flow. The total reactor length, including the side extension tubes, is 64 cm. The JSR is heated

61 by a 30 cm long regulated electrical oven (2×1200 W) that can reach ~1200 K. Thermal

62 isolation of the oven is provided by ceramic wool surrounding it. The temperature along the

63 main axis of the reactor is measured by a movable type K thermocouple. Here, the reactants

64 consisted of high-purity oxygen (99.995% pure, Air Liquide) and high-purity DME (>99.9%

65 pure, Sigma-Aldrich). They were diluted with nitrogen (<100 ppm H_2O, <50 ppm O_2, <1000

66 ppm Ar, <5 ppm H_2, Air Liquide) and mixed just before entering the injectors. The fuel-

67 nitrogen mixture flowed through a fused-silica capillary whereas the O_2/N_2 mixture flowed in

68 the reactor extension tube (Fig. 1). Mass flow controllers (Brooks 5850TR) were used to

69 supply the gases that were preheated before injection to reduce temperature gradients inside

70 the reactor. To determine the concentrations of different species produced during the oxidation

71 process the gas mixture was sampled to the CRDS cell using a fused silica nozzle welded to

72 the JSR (100 μm tip orifice, 53° angle; the tip is located ca. 5 mm inside the JSR).

73

74 (Figure 1)

75

76 The CRDS cell operated at low pressure (0.3 to 10 ±10% mbar) and room temperature

77 whereas the jet-stirred reactor worked at atmospheric pressure. A rotary vane pump was used

78 to withdraw samples from the JSR. The flowrate through the sampling cone ~0.07 dm^3/min

79 was maintained much lower than the total flowrate inside the JSR which ranged from ~1.4 to

80 4.5 dm^3/min. A high precision gauge was used to measure the pressure inside the CRDS cell

81 (Pfeiffer Vacuum TPG 202). The expansion of the gas sample into the CRDS cell causes a

82 pressure drop and cooling which both slow chemical reactions and help detecting highly

83 reactive species such as HO_2. The CRDS cell has a relatively high volume (~3 litres) to limit

84 wall reactions. The connection of the nozzle to the CRDS cell is cooled by circulating a

85 water-ethanol mixture (80:20) at 0-5 °C. This reduces heat transfer from the hot JSR to the

86 CRDS cell and prevents O-ring deterioration.

87 The cw-cavity ring-down spectrometer consisted of two ultra-reflective mirrors (AT Films, 1

88 m radius of curvature, 99.999% reflectivity) mounted on a rectangular cuboid. They were

89 separated by 74 cm to form an optical resonator (Fig.1). A 40 mW continuous laser light

90 source emitted by a DFB laser (~1510 nm, Fitel) was used. The laser diode is tuneable over a

91 3-nm interval using a temperature and current controller (Newport, model 6100). cw-CRDS

92 measurements require frequency matching of the laser emission and a cavity mode. That was

93 done by mounting one of the mirrors onto a piezoelectric transducer fed with a triangular

94 voltage, and modulating the cavity length over a free spectral range. The light escaping from

95 the cavity through the rear mirror was detected by an avalanche photodiode. When the light

96 exceeded a user-defined threshold, the laser beam was deviated using a fibered opto-acoustic

97 modulator (Opto-Electronic). The light intensity decay was recorded as a function of time by

98 a data acquisition card (National Instruments PCI-6111E) with 200 ns time resolution. The

99 ring-down time could then be determined by fitting the exponential decay of the signal

100 (Labview 2010 software, National Instruments Corp.). Typically, 50 ring-down events are

101   recorded and averaged at every wavelength. Figure 2 shows examples of absorption spectra

102   obtained here during the oxidation of DME and earlier during that of n-butane [14] in the

103   wavenumber range 6624-6626 cm^{-1}. One can see from that figure that the recorded spectra are

104   very similar.

105   (Figure 2)

106

107   This is due to the fact that most of the absorption lines correspond to the same intermediates

108   and products ubiquitously formed during the oxidation of hydrocarbons or oxygenates (HO_2,

109   H_2O_2, H_2O, and CH_2O). Ring-down times could then be converted to absorbing species

110   concentrations [S] through:

111

112     $$[S]_t = \frac{L}{d \times c \times \sigma}\left(\frac{1}{\tau_t} - \frac{1}{\tau_0}\right)$$

113

114   where σ is the absorption cross section of S at the absorbing wavelength, L the distance

115   between the two cavity mirrors, d the absorption length over which the absorbing species is

116   present, c is the speed of light, and τ_0 and τ_t are the ring-down times in absence and in

117   presence of S, respectively.

118   (Figure 3)

119

120   The absorption length (d) was obtained by injecting known quantities of methane and

121   acetylene and measuring the absorbance at the centre of the absorption lines at 6623.18 cm^{-1}

122   and 6625.15 cm^{-1}, respectively [19]. For methane, we used absorption cross-sections of 1.54 $\times$

123   10^{-23} cm^2 at 0.35 mbar and 1.48 $\times$ 10^{-23} cm^2 at 10 mbar. For acetylene, we used cross-sections

124   of 7.89 $\times$ 10^{-22} cm^2 at 1 mbar and 6.92 $\times$ 10^{-22} cm^2 at 10 mbar. The measurements were made

125   in presence of a total mirrors protection nitrogen flowrate of 67 cm^3/min. An effective

126 absorption length d= 9±1.5 cm was determined (Figure 3). The absorption cross sections used

127 here are summarized in Table 1. They have been determined in our recent study performed

128 with n-butane under similar conditions[14]. The absorption lines have been selected to avoid

129 interferences with other products in the spectral range available with the laser diode used.

130 Quantifications were made using a resolution of 0.001 cm^{-1}. The absorption cross section of

131 HO_2 derives from previous determinations. Using an average HO_2 air-broadening coefficient

132 of 0.106 cm^{-1}/atm of Tang et al.[20], the HO_2 absorption cross section at 6625.79 cm^{-1} and 0.3

133 mbar was calculated. The latest determination by Tang et al. [20] (30 Torr air), was used to

134 calculate a value of σ=3.16 $\times$ 10^{-19} cm^2 for a line strength of 4.8 $\times$ 10^{-21}. Using the data from

135 Johnson et al.[21] (60 Torr air) and Thiébaud [22] (50 Torr He) enabled to determine Doppler-

136 limited cross sections of 2.45 $\times$ 10^{-19} and 2.58 x 10^{-19} cm^2, respectively. Using the upper-limit

137 value of γ_{air} =0.14 cm^{-1}/atm obtained by Ibrahim et al. [23] yields a cross section of 3.56 $\times$

138 10^{-19}. An average HO_2 absorption cross section of 3 x 10^{-19} cm^2 at 0.3 mbar air associated with

139 an uncertainty of 0.6 $\times$ 10^{-19} cm^2 (i.e. 20%) was then used here.'

140

141   (Table 1)

142

143 For HO_2, a global uncertainty of ~40% was estimated previously [14]. For the other species, it

144 was estimated to be ~20%[14]. Since at low fuel conversion and at 0.3 mbar in the CRDS

145 cell, some stable species are not easily detectable, they were measured at 10 mbar where

146 detection is improved.

147 **3. Results and discussion**

148 The oxidation of DME was performed at atmospheric pressure, at a fixed residence time of

149 1.5 s, and variable temperature (540-850 K), for several initial oxygen and DME

150 concentrations (Table 2).

151

152   (Table 2)

153

154   Figure 4 presents an absorption spectrum recorded during the oxidation of DME.

155   Characteristic absorption lines of HO_2, H_2O_2, H_2O, and CH_2O, in the range 6624 to 6626 cm^{-1}

156   are shown and those used here for the quantitative measurements are identified in red.

157

158   (Figure 4)

159

160   The present results obtained as a function of temperature, at fixed residence time and

161   pressure, are presented in Figures 5-7. For HO_2, error bars are given at 600 K. The data

162   clearly show the two different oxidation regimes of DME, i.e., the cool-flame occurring

163   between ~540-750 K and the high-temperature oxidation regime starting above ~760 K. The

164   maximum cool-flame intensity was observed near 600 K, which is approximately 40 K lower

165   than usually observed for hydrocarbons oxidised under similar conditions[14, 24].

166

167   (Figure 5)

168

169   As expected, the data indicate a reduction of the formation of HO_2 and H_2O_2 when

170   equivalence ratio increases from 1 to 2. Also, the data indicate the two concentration peaks

171   observed for H_2O_2 are of comparable intensity. It seems that the formation of formaldehyde at

172   equivalence ratios of 1 and 2 is less important in the cool-flame than at higher temperature.

173

174   (Figure 6)

175   (Figure 7)

7

176

177 These experiments were simulated using the PSR computer code [25] and three detailed

178 kinetic reaction mechanisms recently published [15, 17]. The mechanism of Burke et al. [15]

179 involved 113 species and 710 reversible reactions. The mechanism of Kurimoto[17] et al.

180 involved 54 species and 293 reversible reactions. The mechanism of Wang et al. [26] involved

181 56 species and 301 reversible reactions. They all include low- and high-temperature oxidation

182 pathways. Figures 5-7 show that the model of Burke et al. [15] represents fairly well the

183 present data. The model of Wang et al. gives acceptable predictions under our experimental

184 conditions. However, the model of Kurimoto et al. [17] seems less accurate (Figure 8). It

185 tends to over-predict DME's oxidation rate (and formation of intermediates) in the cool-flame

186 regime whereas the transition to high-temperature oxidation seems too slow.

187

188 **3. Conclusions and perspectives**

189 A newly developed experimental setup was used for measuring unstable species and other

190 intermediates of DME oxidation at elevated temperatures. The quantitative measurement of

191 HO_2 formed by JSR oxidation of DME at ~550-850 K was performed for the first time by

192 coupling of cw-CRDS and a jet-stirred reactor-sampling nozzle assembly. The concentrations

193 of H_2O_2, H_2O, and CH_2O were also measured using the same technique. The data show the

194 two oxidation regimes of DME: a cool-flame occurs over the temperature range ~540-750 K

195 and the high-temperature oxidation regime starts above ~760 K. The maximum cool-flame

196 intensity was observed near 600 K, which is lower than usually observed for hydrocarbons.

197 The data indicate a reduction of the formation of HO_2 and H_2O_2 when equivalence ratio

198 increases from 1 to 2. The two peaks of concentration observed for H_2O_2 are of comparable

199 intensity whereas the formation of formaldehyde tends to be is less important in the cool-

200 flame than at higher temperature.

201 A kinetic modelling of the present experiments was performed using three recent kinetic

202 models for DME oxidation. One of them represents fairly well the present results whereas the

203 others need some improvements. This new series of experiments further show the usefulness

204 of our experimental set-up that allows the measurement of the concentrations of labile and

205 stable species formed during the oxidation of hydrocarbons and oxygenates.

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