

High Pressure Oxidation of Dimethoxymethane

*Lorena Marrodán, Eduardo Royo, Ángela Millera, Rafael Bilbao, and María U. Alzueta**

Aragón Institute of Engineering Research (I3A). Department of Chemical and Environmental Engineering. University of Zaragoza. 50018 Zaragoza. Spain

* uxue@unizar.es

ABSTRACT

The oxidation of dimethoxymethane (DMM) has been studied under a wide range of temperatures (373-1073 K), pressures (20-60 bar) and air excess ratios ($\lambda=0.7, 1$ and 20), from both experimental and modeling points of view. Experimental results have been interpreted and analyzed in terms of a detailed gas-phase chemical kinetic mechanism for describing the DMM oxidation. The results show that the DMM oxidation regime for 20, 40 and 60 bar is very similar for both reducing and stoichiometric conditions. For oxidizing conditions, a plateau in the DMM, CO and CO₂ concentration profiles as a function of the temperature can be observed. This zone seems to be associated to the peroxy intermediate, CH₃OCH₂O₂, whose formation and consumption reactions appear to be important for the description of DMM conversion under high pressure and high oxygen concentration conditions.

KEYWORDS: dimethoxymethane, high-pressure, oxidation, kinetic model.

Introduction

Diesel engines are used for transportation because of their high fuel efficiency. However, they highly contribute to nitrogen oxides (NO_x) and particulate matter (PM) emissions, which are difficult to reduce simultaneously in conventional diesel engines (NO_x formation is favored under fuel-lean conditions, whereas PM is formed when there is a lack of oxygen). The addition of oxygenated compounds to diesel fuel can effectively reduce these emissions [1-4]. For instance, the reduction of smoke has been reported to be strongly related to the oxygen content of blends [5] without increasing the NO_x and engine thermal efficiency.

Dimethoxymethane (methylal or DMM, CH₃OCH₂OCH₃) is a diether considered to be a potential fuel additive. In comparison to the simplest ether, dimethyl ether (DME), that has been widely proposed and tested for using with diesel fuel as a means of reducing exhaust emissions [6-7], DMM has a higher quantity of oxygen, lower vapor pressure, and better solubility with diesel fuel. Several studies have analyzed the effect of adding DMM to base diesel on emissions of compression ignition engines or direct injection engines (e. g. Ren et al. 2006 [8]) and, in general, diesel-DMM blends increase engine performance and decrease exhaust emissions.

Huang et al. [9] studied the combustion and the emissions of a compression ignition engine fuelled with blends of diesel-DMM. They found that a remarkable reduction in the exhaust CO and smoke can be achieved when operating with diesel-DMM blends, and a simultaneous reduction in both NO_x and smoke can be obtained with large DMM additions. Sathiyagnanam and Saravanan [10] also analyzed the effects of DMM addition to diesel, and obtained an appreciable reduction of emissions such as smoke density, particulate matter, and a marginal increase in the performance when compared with the normal diesel run. Chen et al. [11] developed an experimental and modeling study of the effects of adding oxygenated fuels to

1
2
3 premixed n-heptane flames and found that, as oxygenated fuels were added, mole fractions of
4
5 most C₁-C₅ hydrocarbon intermediates were significantly reduced together with an apparent
6
7 decrease of benzene amount.
8
9

10 Although a great volume of experiments have been conducted to determine the effects of
11
12 diesel-DMM blends in the CO and smoke emissions, few studies have been focused on the
13
14 combustion characteristics of pure DMM fuel at high temperatures [12] and even less at high
15
16 pressures.
17
18

19
20 Daly et al. [13] investigated the oxidation of DMM in a jet-stirred reactor at a pressure of 5.07
21
22 bar, high temperatures of 800-1200 K and equivalence ratios of 0.444 ($\lambda=2.25$), 0.889
23
24 ($\lambda=1.13$) and 1.778 ($\lambda=0.56$), and proposed a sub-mechanism of 50 reactions relevant to
25
26 describe the combustion of DMM, including a significant number of estimated rate constants.
27
28 Recently, Dias et al. [14] have studied lean and rich premixed DMM flames to build a sub-
29
30 mechanism taking into account the formation and the consumption of oxygenated species
31
32 involved in DMM oxidation. They were able to build a new mechanism containing 480
33
34 elementary reactions and involving 90 chemical species, by using kinetic data from the
35
36 literature about DMM, mainly drawn from Daly et al. [13], in order to simulate the DMM
37
38 flames. Whatever the availability of oxygen in the flow, they established two main DMM
39
40 conversion routes, with the first one being the fastest:
41
42
43
44



51 In this context, a study on DMM oxidation carried out under well controlled tubular flow
52
53 reactor conditions at atmospheric pressure, from pyrolysis to high oxidizing conditions, from
54
55 both experimental and modeling points of view, was previously developed by our research
56
57 group [15]. The results obtained indicate that the initial oxygen concentration slightly
58
59
60

1
2
3 influences the consumption of DMM. In general, a good agreement between experimental and
4
5 modeling data was obtained and, accordingly, the final mechanism compiled in that work has
6
7 been taken as the initial mechanism in the present work.
8
9

10 Therefore, the purpose of the present work is to carry out an experimental study of DMM
11
12 conversion at high-pressure covering a large range of temperature, pressure, and different
13
14 stoichiometries, together with the validation of a kinetic mechanism under high-pressure
15
16 conditions, which would be of interest for diesel applications. Specifically, experiments have
17
18 been performed under well-controlled flow reactor conditions, in the 373-1073 K temperature
19
20 range and for different high-pressures (20, 40 and 60 bar). Under these conditions, the oxygen
21
22 concentration was varied from 1960 to 56000 ppm resulting in different air excess ratios (λ),
23
24 ranging from 0.7 to 20. Additionally, a modeling study to describe the oxidation of DMM was
25
26 performed using the gas-phase detailed chemical kinetic mechanism of our previous work
27
28 [15], which has been updated in the present work to account for working at high pressures.
29
30
31
32
33
34
35

36 **Experimental**

37
38
39 The experimental installation used in the present work is described in detail elsewhere [16]
40
41 and only a brief description is given here. It consists basically of a gas feeding system, a
42
43 reaction system and a gas analysis system.
44
45

46
47 Gases are supplied from gas cylinders through mass flow controllers. A concentration of
48
49 approximately 700 ppm of DMM is introduced in all the experiments. The amount of O₂ used
50
51 has been varied between 1960 and 56000 ppm, and is related to the air excess ratio (λ),
52
53 defined as the inlet oxygen concentration divided by the stoichiometric oxygen. Therefore,
54
55 values of λ lower than 1 refer to fuel rich conditions, and λ values larger than 1, refer to fuel
56
57
58
59
60

1
2
3 lean conditions. Nitrogen is used to balance, resulting in a constant flow rate of 1000 (STP)
4
5 mL/min.
6

7
8 The DMM oxidation takes place in a quartz flow reactor (inner diameter of 6 mm and 1500
9
10 mm in length) that is enclosed in a stainless steel tube that acts as a pressure shell. Nitrogen is
11
12 delivered to the shell side of the reactor by a pressure control system, to obtain a pressure
13
14 similar to that inside the reactor avoiding this way the stress in the reactor.
15
16

17
18 The reactor tube is placed horizontally in a three-zone electrically heated furnace, ensuring a
19
20 uniform temperature profile within ± 10 K throughout the isothermal reaction zone (56 cm).
21

22 The gas residence time, t_r , in the isothermal zone, is a function of the reaction temperature and
23
24 pressure, $t_r(\text{s}) = 261 * P(\text{bar}) / T(\text{K})$.
25
26

27
28 Downstream the reactor, the pressure is reduced to atmospheric level. Before analysis, the
29
30 product gases pass through a condenser and a filter to ensure gas cleaning. The outlet gas
31
32 composition is measured using a gas micro chromatograph (Agilent 3000), which is able to
33
34 detect and measure DMM and the main products of its oxidation: methyl formate
35
36 (CH_3OCHO), formaldehyde (CH_2O), CO , CO_2 and CH_4 . No other products were detected in a
37
38 noticeable amount. The uncertainty of measurements is estimated as $\pm 5\%$. To evaluate the
39
40 goodness of the experiments, the atomic carbon balance was checked in all the experiments
41
42 and resulted to close always near 100%.
43
44

45
46 The experiments were carried out at different pressures (20, 40 and 60 bar) and in the 373-
47
48 1073 K temperature range. Table 1 lists the conditions of the experiments.
49
50

Modeling

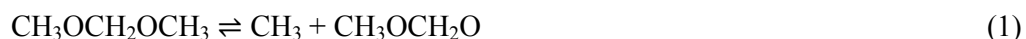
The experimental results have been analyzed in terms of a detailed gas-phase chemical kinetic mechanism for describing the oxidation of DMM. The model taken as starting point was the kinetic mechanism compiled in the previously appointed work about the DMM oxidation at atmospheric pressure by our research group [15]. This one was built by adding different reaction subsets found in the literature to the model developed by Glarborg et al. [17] updated and extended later [18, 19]. The additional reaction subsets included for the different expected or involved compounds of relevance for the present experiments were: dimethyl ether (DME) [20], ethanol [21], acetylene [22], and methyl formate (MF) [23]. The last one subset was revised by our group [16] to account for high-pressure conditions in the methyl formate oxidation, which are similar to those of the present work. For DMM, the Dias et al. reaction subset [14] developed for atmospheric pressure was also included. Thermodynamic data for the involved species are taken from the same sources as the cited mechanisms.

The model used in the previous work [15] has been modified in the present work to account also for the high-pressure conditions studied in the DMM oxidation. The changes made to the mechanism are listed in Table 2 and will be described below. The final mechanism involves 726 reactions and 142 species.

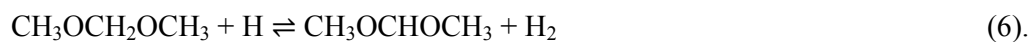
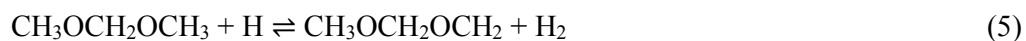
Thermal decomposition of DMM is an important initiation step, and can occur through DMM breaking, reactions 1 and 2, or by losing a primary or a secondary hydrogen atom, reactions 3 and 4 respectively. The constants for these reactions were kept, without any modification, from the work of Dias et al. [14], originally proposed by Daly et al. [13].

For reaction 1, the value of $2.62 \times 10^{16} \exp(-41369/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the rate constant was taken from the estimation made by Dagaut et al. [24] for DME, from a fit of the available NIST [25] data. For reaction 2, the value for the rate constant, $2.51 \times 10^{15} \exp(-38651/T) \text{ cm}^3$

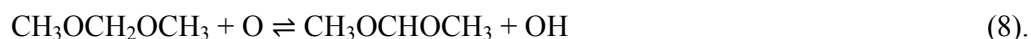
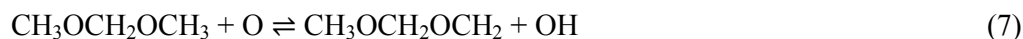
1
2
3 mol⁻¹ s⁻¹, estimated by Foucaut and Martin by analogy with diethylether [26] was taken, and
4
5 for reaction 3, the kinetic parameters ($4.35 \times 10^{16} \exp(-50327/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) were taken
6
7 from the estimation for the similar reaction involving ethane [27]. Finally, for the loss of a
8
9 secondary hydrogen atom from DMM, reaction 4, Dean [27] estimated the rate constant by
10
11 analogy with the rate constant for the loss of a secondary atom of hydrogen from propane,
12
13 with a value of $6.31 \times 10^{15} \exp(-47660/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
14
15



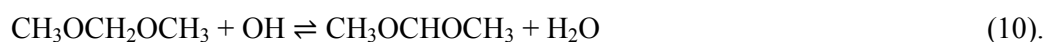
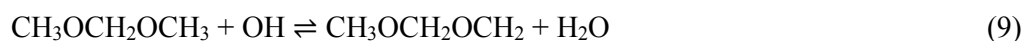
28
29 An important pathway for DMM consumption includes hydrogen abstraction reactions by the
30
31 O/H radical pool. For the reactions with H (reactions 5 and 6), the rate expressions were taken
32
33 from the DMM subset proposed by Dias et al. [14], which were, a priori, taken from Daly et
34
35 al. [13]. The rate constant of reaction 5 was taken as that for the reaction between DME and a
36
37 hydrogen atom [28], that is $9.70 \times 10^{13} \exp(-3125/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. For reaction 6, the $7.40 \times$
38
39 $10^{12} \exp(-1631/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ rate constant was based on the abstraction of a secondary
40
41 hydrogen atom from diethylether [29]. Although, Dias et al. [14] included an A-factor for this
42
43 reaction divided by 2 in their final mechanism, we adopted the value originally proposed by
44
45 Daly et al. [13], which is $7.40 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.
46
47
48



1
2
3 In the case of the reactions between DMM and O radicals (reactions 7 and 8), their rate
4 constants were taken from the DMM subset proposed by Dias et al. [14] without any
5 modification, previously adopted from [30], by analogy with CH₃OCH₂ for reaction 7, and by
6 analogy with diethylether, for reaction 8.
7
8
9
10

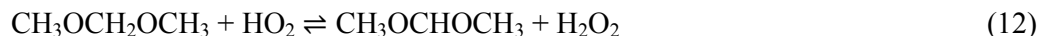
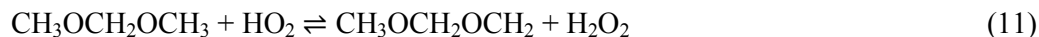


13
14
15
16
17
18
19 Reaction with hydroxyl radicals (OH) is an important step in the oxidation of organic
20 compounds in combustion systems [31]. Although it will be discussed later through the
21 analysis of the different reaction pathways, the main consumption of DMM occurs through H
22 abstraction reactions by OH to form CH₃OCH₂OCH₂ and CH₃OCHOCH₃ radicals (reactions
23 9 and 10). The kinetic parameters of these reactions have been modified from the previous
24 work [15].
25
26
27
28
29
30
31



34
35
36
37
38
39 In the Dias et al. DMM reaction subset [14], the rate constant of these reactions is estimated
40 by analogy with the reaction CH₃OCH₃ + OH = CH₃OCH₂ + H₂O from DeMore and Bayes
41 [32], with a proposed value of $9.10 \times 10^{12} \exp(-496/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, determined
42 experimentally in the 263-361 K temperature range. Arif et al. [31] determined a rate constant
43 of $6.32 \times 10^6 T^2 \exp(327/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, in the 295-650 K temperature range, which is
44 adopted in this study, also used in the work of Alzueta et al. [20], and that is in agreement
45 with the high-temperature (923-1423 K) determination of Cook et al. [33]. With this value,
46 the latest authors achieved a good fit for both the low and the high temperature measurements.
47
48
49
50
51
52
53
54
55
56
57
58
59
60

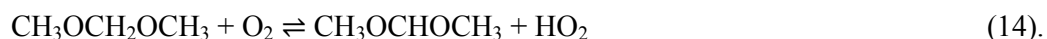
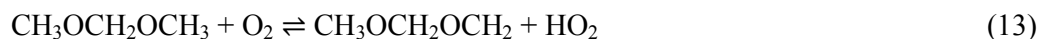
1
2
3 The prevalence of HO₂ radicals under high pressure, and preferably lean conditions, should
4 make them to play an important role under the conditions of the present work. Reactions
5 involving DMM and HO₂ radicals (reactions 11 and 12) were not included in the initial
6 reaction subset of Dias et al. [14], and we have included them in the present work,
7
8
9



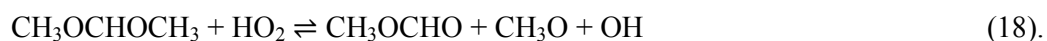
19 The rate constants for reactions 11 and 12 have not been measured to our knowledge and,
20 therefore, there is some degree of uncertainty in their absolute values. For reaction 11, the rate
21 parameters have been taken by analogy of the dimethyl ether and HO₂ reaction, following the
22 same procedure described by Daly et al. [13], and likewise taking the value, $1.00 \times 10^{13} \exp(-$
23 $8900/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, from the work of Curran et al. [34]. The rate constant for abstraction of
24 a secondary hydrogen atom (reaction 12) was estimated by Daly et al. [13] from the value for
25 reaction 11, with the A factor divided by a factor of 6. These authors stated that DMM has six
26 primary hydrogen atoms and only two secondary ones, so the probability of attack will
27 therefore be lower for the attack on the CH₂ groups than on the CH₃ groups. Also, the
28 proximity of two oxygen atoms to the central carbon atom of the molecule will make the
29 hydrogen atoms attached to it more labile than those belonging to the methyl groups. As a
30 result, the activation energy for reaction 12 should be lower than for reaction 11. Thus, a rate
31 constant value of $2.00 \times 10^{12} \exp(-7698/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ was proposed for reaction 12 [13],
32 which is adopted in the present mechanism.
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49

50 The subset proposed by Dias et al. [14] includes reactions involving DMM with molecular
51 oxygen (reaction 13 and 14) and their corresponding rate constants, adopted here with no
52 modification from the work of Daly et al. [13], were both estimated by analogy with the
53 reaction of DME with oxygen. Therefore, the rate parameters for reaction 13 are the same as
54
55
56
57
58
59
60

those considered by Dagaut et al. [24] (although for reaction 13, the values used by Dias et al. [14] are not the corresponding ones to the source specified, as also was indicated in the case of reaction 6), and the parameters for reaction 14 were estimated by Daly et al. [13] as previously done in the case of reactions involving HO₂ radicals.



Although the reactions of CH₃OCH₂OCH₂ and CH₃OCHOCH₃ radicals with O₂ (reactions 15 and 16) and HO₂ (reactions 17 and 18) were omitted in previous DMM mechanisms [14, 15, 34], they can play an important role in the oxidation of DMM, particularly under high pressure and high oxygen concentration conditions and, therefore, these reactions have been included in our final mechanism.



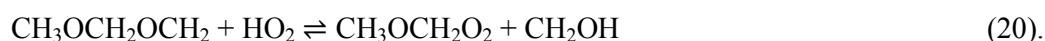
For reactions 15 and 16, the rate constants have been estimated establishing an analogy with the reaction of methoxy-methyl radical (CH₃OCH₂, generated in the dimethyl ether thermal decomposition) and oxygen molecular, as previously done by Daly et al. [13]. In that case, they chose the kinetic parameters given by Dagaut et al. [24]; namely, $1.70 \times 10^{10} \exp(337/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which were estimated based on C₂H₅ + O₂ kinetics. However, here, we have chosen a value of the CH₃OCH₂ + O₂ rate constant of $2.50 \times 10^{11} \exp(850/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, obtained by Alzueta et al. [20] from averaging three room-temperature determinations [35-

37], and adopting the temperature dependence reported in Hoyermann and Nacke [37], which is significantly faster than that proposed in the mechanism of Dagaut et al. [24].

In the same way, the analogy used before in the case of reactions with molecular oxygen ($\text{CH}_3\text{OCH}_2 + \text{O}_2$) has been applied to obtain the rate constants of reactions 17 and 18, i.e. $\text{CH}_3\text{OCH}_2 + \text{HO}_2$. Not much information has been found related to these reactions, and the value proposed by Daly et al. [13], based on estimations made by Dagaut et al. [24] has been chosen. This value is, for reaction 17, $3.00 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and, for reaction 18 they increased this value to $1.00 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Curran et al. [34] stated that the pathway involving peroxy intermediates may be important at low temperatures (below approximately 900 K) and pressures higher than 10 bar, because the bimolecular addition of methoxy-methyl radical to O_2 has a lower activation energy barrier than the β -scission to yield CH_2O and CH_3 , the two main pathways that methoxy-methyl radicals can undergo. At atmospheric pressure (e.g. Alzueta et al. [20]), the formation of methoxy methyl-peroxy intermediate is not predicted to be significant, except for a minor contribution for very lean stoichiometries.

Under the conditions studied in this work, high pressures (20, 40 and 60 bar) and fuel lean conditions ($\lambda=20$), the reactions forming peroxy species (reactions 19 and 20) may have an important impact on the oxidation chemistry of DMM and, therefore, these reactions have been included in our final mechanism.



For reaction 19, the kinetic parameters have been estimated by analogy with the reaction of methoxy-methyl radical with molecular oxygen. The $6.40 \times 10^{12} \exp(-45.80/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

1
2
3 value for $\text{CH}_3\text{OCH}_2 + \text{O}_2$ was considered in an earlier mechanism by our group [20]. For
4
5 reaction 20, no values of kinetic parameters were found, and we have considered initially a
6
7 reaction rate of $1.0 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The results of sensitivity analysis, shown later,
8
9 indicate no significant impact of this estimation.
10

11
12 Model calculations have been performed using both SENKIN [38] from the CHEMKIN II
13
14 software package [39] and CHEMKIN-PRO [40], considering pressure constant in the
15
16 reaction zone and the corresponding temperature profile. An example of temperature profiles
17
18 inside the reactor can be found in [16]. The full mechanism listing and thermochemistry used
19
20 can be found as Supporting Information.
21
22
23
24
25
26

27 **Results and discussion**

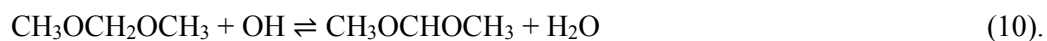
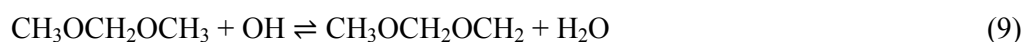
28
29
30 In this work, a study of the oxidation of DMM at different pressures (20, 40 and 60 bar), and
31
32 in the 373-1073 K temperature range, has been carried out. In addition to temperature and
33
34 pressure, the influence of stoichiometry ($\lambda=0.7$, 1 and 20) on the oxidation process has also
35
36 been analyzed. As mentioned, the experimental results have been interpreted in terms of the
37
38 detailed kinetic mechanism previously described.
39
40
41

42
43 Figures 1 and 2 show the influence of the temperature and pressure for specific air excess
44
45 ratios, $\lambda=0.7$ and $\lambda=1$, respectively, on the concentration of DMM and the formation of the
46
47 main products of its oxidation at high pressures: CH_2O , CO_2 , CO , CH_3OCHO and CH_4 . No
48
49 other products have been detected in an appreciable amount. At atmospheric pressure, other
50
51 products such as C_2H_4 , C_2H_6 and C_2H_2 , were detected through micro GC analysis in amounts
52
53 lower than 100 ppm, and especially for reducing ($\lambda=0.7$), very reducing ($\lambda=0.4$) and pyrolysis
54
55 ($\lambda=0$) conditions [15]. Methanol is highly formed at atmospheric pressure [15], while at
56
57
58
59
60

1
2
3 higher pressures (20-60 bar) formaldehyde is predominant, although the distinction between
4
5 methanol and formaldehyde with micro-GC techniques sometimes is quite tricky.
6
7

8 Both Figures 1 and 2 compare experimental (symbols) and model calculation (lines) results.
9
10 Working at 20, 40 or 60 bar, does not have a big effect neither on the oxidation of DMM nor
11
12 on the formation of the main products. The suggested model predicts the general trend of the
13
14 different concentration profiles, although there are some discrepancies between experimental
15
16 and simulation results. These discrepancies are especially remarkable for $\lambda=0.7$, where the
17
18 CO_2 concentration values at high temperatures are underestimated, whereas the CO values are
19
20 overestimated. It is difficult to isolate the origin of those discrepancies, and may be attributed
21
22 to the uncertainty in the conversion of intermediates. This fact is not observed for the other
23
24 values of λ considered. The oxygen concentration in the reactant mixture slightly influences
25
26 the conversion of DMM, similar to what has been observed in the oxidation behavior of other
27
28 oxygenated compounds such as DME [20] or MF [16].
29
30
31
32

33 Figure 3 shows a reaction path diagram for DMM oxidation through a reaction rate analysis
34
35 with the mechanism used in the present work. For the conditions analyzed in the present
36
37 work, the main consumption of DMM is through H abstraction reactions by the hydroxyl
38
39 radical (OH) to form $\text{CH}_3\text{OCH}_2\text{OCH}_2$ and $\text{CH}_3\text{OCHOCH}_3$ radicals (reactions 9 and 10),
40
41 which is in agreement with other previous works [13]. Both reactions have a relative
42
43 importance of 38%. This value increases up to near 50% under oxidizing conditions.
44
45
46



51
52
53 Both radicals react with molecular oxygen to form methyl formate (CH_3OCHO) and
54
55 formaldehyde as main products:
56
57
58
59
60



Formaldehyde continues the $\text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{CO} \rightarrow \text{CO}_2$ reaction sequence with CO_2 as final product. As shown in Figure 3, MF seems to be an important intermediate in the total oxidation of DMM. In previous MF oxidation works, at atmospheric pressure [23] and higher pressures [16], the MF oxidation was seen to be initiated by its decomposition reaction to methanol (reaction 21). In this work, as an intermediate, MF is directly consumed by hydrogen abstraction reactions in order to produce CH_2OCHO and CH_3OCO radicals (reactions 22 and 23), with a relative importance, for example at 20 bar and oxidizing conditions ($\lambda=20$), of 62% for reaction 22 and 20% for reaction 23.



Both radicals decompose thermally, CH_2OCHO to give formaldehyde and formyl radical and CH_3OCO to form methyl radical and CO_2 , through reactions 24 and 25, respectively:



As reported in an earlier work by our group for methyl formate oxidation [16], under high-pressure conditions, high concentration of methyl and hydroperoxy radicals accumulate and thus, the interaction of those radicals can generate methoxy radicals through reaction 26, which further decomposes to formaldehyde (reaction 27).





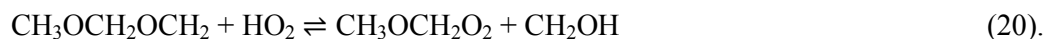
Therefore, formaldehyde is detected instead of methanol (highly formed in both MF oxidation [23] and DMM oxidation [15] at atmospheric pressure) when working under high pressure.

The formaldehyde obtained by this way continues the above mentioned $\text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{CO} \rightarrow \text{CO}_2$ reaction sequence. A fraction of this formaldehyde reacts with methyl radicals generating methane (reaction 28), which is detected as final product.



Figure 4 shows the influence of pressure on the DMM, CO_2 , CO , CH_2O and MF concentration profiles as a function of temperature and for very oxidizing conditions, $\lambda=20$. As previously seen, working under high pressure conditions no appreciable influence of pressure on the conversion regime of DMM and products formation is found. Thus, similar results have been obtained for 20, 40 and 60 bar, and the slight differences that can be observed include a higher amount of methyl formate for 20 bar, while for the other two values of pressure, more CO_2 is produced. For the pressures of 40 and 60 bar, in the 598-673 K temperature range, a constant concentration zone in the DMM profile and in the main products, CO_2 , CO , CH_3OCHO and CH_2O , can be observed. This zone appears to be associated to the oxygenated $\text{CH}_3\text{OCH}_2\text{O}_2$ species. In the mechanism taken as starting point and used in the previous atmosphere work on DMM conversion [15], the formation reactions of this species were not included, and thus the predictions of the mechanism were significantly worse. Therefore, the formation reactions of this species from the interaction of $\text{CH}_3\text{OCH}_2\text{OCH}_2$ and O_2/HO_2 (active species under oxidizing and high pressure conditions), reactions 19 and 20, were added to the mechanism:





6 With these two reactions, the current mechanism has been able to represent the plateau
7 observed in DMM, CO_2 and CO concentration, in the 598-673 K temperature range. The
8 kinetic parameters of these reactions have been estimated due to the lack of literature
9 determinations above mentioned, as has been described in the Modeling section. Reaction
10 pathway analysis allows us to identify how the species are formed and proceed through the
11 following reaction sequence: $\text{CH}_3\text{OCH}_2\text{O}_2 \rightarrow \text{CH}_2\text{OCH}_2\text{O}_2\text{H} \rightarrow \text{O}_2\text{CH}_2\text{OCH}_2\text{O}_2\text{H} \rightarrow$
12 $\text{HO}_2\text{CH}_2\text{OCHO} \rightarrow \text{OCH}_2\text{OCHO}$. The last one decomposes to give CH_2O and HCOO through
13 reaction 29:
14
15
16
17
18
19
20
21
22



27 Formaldehyde continues the $\text{CH}_2\text{O} \rightarrow \text{HCO} \rightarrow \text{CO} \rightarrow \text{CO}_2$ well-known reaction sequence,
28 whereas the hydrocarboxyl radical decomposes generating CO_2 as final product:
29
30
31



36 A first-order sensitivity analysis for CO has been performed for all the sets in Table 1. The
37 results obtained, shown in Table 3, indicate that the conversion of DMM is highly sensitive to
38 the DMM reactions with OH radicals (reactions 9 and 10), which have been previously
39 discussed. Reactions involving MF (CH_3OCHO) and its radicals also present a high
40 sensitivity, as an important intermediate in the DMM oxidation under the conditions studied
41 in the present work.
42
43
44
45
46
47
48

49 Figure 5 shows the experimental results obtained for stoichiometric conditions by our
50 research group for the DMM oxidation at atmospheric pressure [15] and the high-pressure
51 results, experimental and modeling, discussed in the present work. Although it can be
52 observed a huge shift to lower temperatures when moving from atmospheric pressure to
53
54
55
56
57
58
59
60

1
2
3 higher ones, the results can not be directly compared because both gas residence times are
4 significantly different. The gas residence time for the high pressure installation
5 ($t_r(s)=261 \cdot P(\text{bar})/T(\text{K})$) is longer than at atmospheric pressure ($t_r(s)=195/T(\text{K})$) by a factor of
6
7
8
9
10 27-80 and, therefore, it is not possible to distinguish between the effect of pressure or
11 residence time. To overcome this problem, model calculations have been carried out,
12
13 modifying either the residence time or the pressure input value.
14
15

16
17 To do this, the kinetic mechanism used to simulate the high pressure experiments of this work
18 has also been used to simulate the results obtained in the DMM oxidation at atmospheric
19 pressure [15].
20
21
22

23
24 Figure 6 shows, as an example, a comparison (only for DMM, CO and CO₂ concentrations)
25 between the modeling results obtained with the initial mechanism [15] (dashed lines) or with
26 the mechanism modified in the present work (solid lines) and the experimental results
27 (symbols) attained at atmospheric pressure in the 573-1373 K temperature range, for an initial
28 concentration of 700 ppm of DMM and stoichiometric conditions [15]. N₂ was used to
29 achieve a total flow rate of 1000 mL(STP)/min, resulting in a gas residence time dependent of
30 the reaction temperature of $t_r(s)=195/T(\text{K})$ [15]. As can be seen in Figure 6, the modified
31 mechanism generates almost the same results of the mechanism of reference [15] and thus is
32 able to predict the main trends of the DMM consumption profile and CO and CO₂ formation.
33
34
35
36
37
38
39
40
41
42
43
44

45 With the validated kinetic mechanism of the present work, that describes well both low and
46 high pressure experimental results, we have made different simulations to try to distinguish
47 between the effect of residence time or pressure.
48
49
50

51
52 Figure 7 includes calculations for $\lambda=1$ and 20 bar, with a residence time of $t_r(s)=5220/T(\text{K})$
53 (solid lines) and for the same conditions ($\lambda=1$ and 20 bar) but for a lower residence time of
54 $t_r(s)=261/T(\text{K})$ (short dashed lines), which would be the same as the residence time
55
56
57
58
59
60

1
2
3 corresponding to 1 bar. As a reference, in Figure 7, also the experimental data of set 4 in
4
5 Table 1 are included ($\lambda=1$, 20 bar) and denoted by symbols. As can be seen, when only
6
7 residence time is changed, increasing residence time shifts significantly the conversion of
8
9 DMM towards lower temperatures.
10

11
12 Additionally, Figure 7 also includes calculations made with 1 bar of pressure and the
13
14 residence time of the 20 bar experiments, i.e. $t_r(s)=5220/T(K)$ (long-dashed lines). Increasing
15
16 pressure from 1 bar (long-dashed lines) to 20 bar (solid lines) but keeping a given residence
17
18 time of $t_r(s)=5220/T(K)$ results in a similar shift of the DMM concentration profile as that
19
20 reported for the change in time residence.
21
22

23
24 Thus, both the pressure and the residence time have an appreciable impact and are responsible
25
26 for a significant shift in the oxidation regime of DMM.
27
28
29
30
31

32 33 **Conclusions** 34

35
36 The DMM conversion has been investigated in a quartz flow reactor in the 373-1073 K
37
38 temperature range, for different air excess ratios ($\lambda=0.7$, 1 and 20) and pressures (20-60 bar).
39
40 The experimental results have been interpreted in terms of a detailed kinetic mechanism,
41
42 compiled in a previous work about the DMM oxidation at atmospheric pressure by our
43
44 research group [15], and modified in the present work to account also for the high pressure
45
46 conditions studied. The modeling results obtained with the modified mechanism are similar to
47
48 those attained without any modification; that is, the new mechanism is able to predict the
49
50 main trends observed for the DMM oxidation at atmospheric pressure.
51
52

53
54 Experimental results and model calculations are, in general, in good agreement, and the main
55
56 trends are well predicted for the theoretical model. Slight differences are noticed when
57
58
59
60

1
2
3 working under stoichiometric or somewhat fuel-rich conditions, although the DMM
4
5 conversion is a bit different for oxidizing conditions. Working at 20, 40 or 60 bar does not
6
7 have a big effect on neither the oxidation of DMM nor the formation of the main products.
8
9

10 Independently of the conditions (stoichiometric, oxidizing or reducing), the main
11
12 consumption of DMM occurs through H abstraction reactions by the hydroxyl radical (OH).
13

14 Under oxidizing conditions, the conversion of DMM is fast until approximately the 598 to
15
16 673 K temperature zone, where the concentration of DMM presents a plateau and remains
17
18 constant. This zone appears to be associated to the formation of the intermediate $\text{CH}_3\text{OCH}_2\text{O}_2$
19
20 oxygenated species. The formation reactions of this species from the interaction of
21
22 $\text{CH}_3\text{OCH}_2\text{OCH}_2$ and O_2/HO_2 , active species under oxidizing and high pressure conditions,
23
24 were not initially considered in the DMM reaction subset taken from the literature [14].
25
26

27 Therefore, these reactions were added to the mechanism.
28
29

30
31 The analysis of the main reaction pathways involved in the DMM conversion, occurring
32
33 under the conditions studied in the present work, has shown that methyl formate plays an
34
35 important role in this process.
36
37

38 The experimental results obtained under high-pressure conditions in the present work are
39
40 shifted towards lower temperatures compared to those obtained at atmospheric pressure by
41
42 Marrodán et al. [15], for different residence times. Model calculations have been performed to
43
44 evaluate independently the effect of pressure and gas residence time and results indicate that
45
46 both variables have remarkable influence on the DMM oxidation process.
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Acknowledgements

The authors express their gratitude to the Aragón Government (GPT group) and to MINECO and FEDER (Project CTQ2012-34423), for financial support.

Supporting Information

The full mechanism listing including the thermodynamic data additional to THERMDAT [41]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- [1] Zhu, R.; Wang, X.; Miao, H.; Yang, X.; Huang, Z. *Fuel* **2011**, 90, 1731-1737.
- [2] Vertin, K.D.; Ohi, J.M.; Naegeli, D.W.; Childress, K.H.; Hagen, G.P.; McCarthy, C.I.; Cheng, A.S.; Dibble, R.W. *SAE technical paper* 1999-01-1508, **1999**.
- [3] Yanfeng, G.; Shenghua, L.; Hejun, G.; Tiegang, H.; Longbao, Z. *Appl. Therm. Eng.* **2007**, 27, 202-207.
- [4] Zhu, R.; Miao, H.; Wang, X.; Huang, Z. *Proc. Combust. Inst.* **2013**, 34, 3013-3020.
- [5] Ren, Y.; Huang, Z.; Miao, H.; Di, Y.; Jiang, D.; Zeng, K.; Liu, B.; Wang, X. *Fuel* **2008**, 87, 2691-2697.
- [6] Ying, W.; Longbao, Z.; Hewu, W. *Atmos. Environ.* **2006**, 40, 2313-2320
- [7] Arcoumanis, C.; Bae, C.; Crookes, R.; Kinoshita, E. *Fuel* **2008**, 87, 1014-1030.
- [8] Ren, Y.; Huang, Z.; Jiang, D.; Liu, L.; Zeng, K.; Liu, B.; Wang, X. *Appl. Therm. Eng.* **2006**, 26, 327-337.
- [9] Huang, Z.H.; Ren, Y.; Jiang, D.M.; Liu, L.X.; Zeng, K.; Liu, B.; Wang, X.B. *Energy Convers. Manage.* **2006**, 47, 1402-1415.
- [10] Sathiyagnanam, A.P.; Saravanan, C.G. *Fuel* **2008**, 87, 2281-2285.

- 1
2
3 [11] Chen, G.; Yu, W.; Fu, J.; Mo, J.; Huang, Z.; Yang, J.; Wang, Z.; Jin, H.; Qi, F.
4
5 *Combust. Flame* **2012**, 159, 2324-2335.
6
7 [12] Zhang, C.; Li, P.; Li, Y.; He, J.; Li, X. *Energy Fuels* **2014**, 28, 4603-4610.
8
9 [13] Daly, C.A.; Simmie, J.M.; Dagaut, P.; Cathonnet, M. *Combust. Flame* **2001**, 125,
10 1106-1117.
11
12 [14] Dias, V.; Lories, X.; Vandooren, J. *Combust. Sci. Technol.* **2010**, 182, 350-364.
13
14 [15] Marrodán, L.; Monge, F.; Millera, A.; Bilbao, R.; Alzueta, M.U. (*Accepted for*
15 *presentation in the Ninth Mediterranean Combustion Symposium, Rhodes, Greece,*
16 *June 2015*)
17
18 [16] Marrodán, L.; Millera, A.; Bilbao, R.; Alzueta, M.U. *Energy Fuels* **2014**, 28, 6107-
19 6115.
20
21 [17] Glarborg, P.; Alzueta, M.U.; Dam-Johansen, K.; Miller, J.A. *Combust. Flame* **1998**,
22 115, 1-27.
23
24 [18] Glarborg, P.; Alzueta, M.U.; Kjærgaard, K.; Dam-Johansen, K. *Combust. Flame* **2003**,
25 132, 629-638.
26
27 [19] Skjøth-Rasmussen, M.S.; Glarborg, P.; Østberg, M.; Johannessen, J.T.; Livbjerg, H.;
28 Jensen, A.D.; Christensen, T.S. *Combust. Flame* **2004**, 136, 91-128.
29
30 [20] Alzueta, M.U.; Muro, J.; Bilbao, R.; Glarborg, P. *Isr. J. Chem.* **1999**, 39, 73-86.
31
32 [21] Alzueta, M.U.; Hernández, J.M. *Energy Fuels* **2002**, 16, 166-171.
33
34 [22] Alzueta, M.U.; Borruy, M.; Callejas, A.; Millera, A.; Bilbao, R. *Combust. Flame*
35 **2008**, 152, 377-386
36
37 [23] Alzueta, M.U.; Aranda, V.; Monge, F.; Millera, A.; Bilbao, R. *Combust. Flame* **2013**,
38 160, 853-860.
39
40 [24] Dagaut, P.; Boettner, J.C.; Cathonnet, M. *Proc. Combust. Inst.* **1996**, 26, 627-632.
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 [25] Mallard, W.G.; Westley, F.; Herron, J.T.; Hampson, R.F. *NIST Chemical Kinetics*
4
5 *Database 6.01* **1994**.
6
7 [26] Foucaut, J.F.; Martin, R. *J. Chim. Phys.* **1978**, 75, 132-144.
8
9 [27] Dean, A.M. *J. Phys. Chem.* **1985**, 89, 4600-4608.
10
11 [28] Dagaut, P.; Daly, C.; Simmie, J.M.; Cathonnet, M. *Proc. Combust. Inst.* **1998**, 27, 361-
12
13 369.
14
15 [29] Faubel, C.; Hoyermann, K.; Strofer, E.; Wagner, H. *Ber Bunsenges Phys. Chem.* **1979**,
16
17 83, 532-538.
18
19 [30] Herron, J.T. *J. Phys. Chem. Ref. Data* **1988**, 17, 967-1026.
20
21 [31] Arif, M.; Dellinger, B.; Taylor, P.H. *J. Phys. Chem. A* **1997**, 101, 2436-2441.
22
23 [32] DeMore, W.B.; Bayes, K.D. *J. Phys. Chem. A* **1999**, 103, 2649-2654.
24
25 [33] Cook, R.D.; Davidson, D.F.; Hanson, R.K. *J. Phys. Chem. A* **2009**, 113, 9974-9980.
26
27 [34] Curran, H.J.; Pitz, W.J., Westbrook, C.K.; Dagaut, P.; Boettner, J.C.; Cathonnet, M.
28
29 *Int. J. Chem. Kinet.* **1998**, 30, 229-241.
30
31 [35] Sehested, J.; Sehested, K.; Platz, J.; Egsgaard, H.; Nielsen, O.J. *Int. J. Chem. Kinet.*
32
33 **1997**, 29, 627-637.
34
35 [36] Sehested, J.; Mogelberg, T.; Wallington, T.J.; Kaiser, E.W.; Nielsen, O.J. *J. Phys.*
36
37 *Chem.* **1996**, 100, 17218-17225.
38
39 [37] Hoyerman, K.; Nacke, F. *Proc. Combust. Inst.* **1996**, 26, 505-512.
40
41 [38] Lutz, A.E.; Kee, R.J.; Miller, J.A. *SENKIN: A FORTRAN Program for Predicting*
42
43 *Homogeneous Gas Phase Chemical Kinetics with Sensitivity Analysis*; Sandia National
44
45 Laboratories: Livermore, CA, **1988**; Report SAND87-8248.
46
47 [39] Kee, R.J.; Rupley, F.M.; Miller, J.A. *CHEMKIN-II: A FORTRAN Chemical Kinetics*
48
49 *Package for the Analysis of Gas-Phase Chemical Kinetics*; Sandia National
50
51 Laboratories: Albuquerque, NM, **1991**; Report SAND87-8215.
52
53
54
55
56
57
58
59
60

1
2
3 [40] CHEMKIN-PRO, Release 15131, Reaction Design, San Diego, **2013**.
4

5 [41] Burcat, A.; Ruscic, B. *Third Millennium Ideal Gas and Condensed Phase*
6
7 *Thermochemical Database for Combustion with Updates from Active Thermochemical*
8
9 *Tables*, Report TAE960, Technion Israel Inst. of Technology, 16th September 2005.
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Table captions

Table 1. Matrix of experimental conditions. The experiments are conducted at constant flow rate of 1000 mL(STP)/min, in the temperature interval of 373-1073 K. The balance is closed with N₂. The residence time depends on the reaction temperature and pressure: $t_r(\text{s})=261 \cdot P(\text{bar})/T(\text{K})$.

Table 2. Reactions modified or included in the final mechanism in relation to the mechanism used in reference [15] and corresponding kinetic parameters.

Table 3. Linear sensitivity coefficients for CO for sets 1-9 in Table 1. The sensitivity coefficients are given as $A_i \delta Y_j / Y_j \delta A_i$, where A_i is the pre-exponential constant for reaction i and Y_j is the mass fraction of j th species. Therefore, the sensitivity coefficients listed can be interpreted as the relative change in predicted concentration for the species j caused by increasing the rate constant for reaction i by a factor of 2.

Tables**Table 1.**

Matrix of experimental conditions. The experiments are conducted at constant flow rate of 1000 mL(STP)/min, in the temperature interval of 373-1073 K. The balance is closed with N₂. The residence time depends on the reaction temperature and pressure: $t_r(\text{s})=261 \cdot P(\text{bar})/T(\text{K})$.

Exp.	DMM (ppm)	O₂ (ppm)	λ	P (bar)
Set 1	720	1960	0.7	20
Set 2	770	1960	0.7	40
Set 3	770	1960	0.7	60
Set 4	757	2800	1	20
Set 5	720	2800	1	40
Set 6	720	2800	1	60
Set 7	688	56000	20	20
Set 8	778	56000	20	40
Set 9	706	56000	20	60

Table 2.

Reactions modified or included in the final mechanism in relation to the mechanism used in reference [15] and corresponding kinetic parameters.

Number	Reaction	A	n	E _a	Source
9	$\text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_2\text{OCH}_2 + \text{H}_2\text{O}$	6.32×10^6	2.00	-652	[22, 32, 34, see text]
10	$\text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{OH} \rightleftharpoons \text{CH}_3\text{OCHOCH}_3 + \text{H}_2\text{O}$	6.32×10^6	2.00	-652	[22, 32, 34, see text]
11	$\text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{OCH}_2\text{OCH}_2 + \text{H}_2\text{O}_2$	1.00×10^{13}	0.00	17686	[35]
12	$\text{CH}_3\text{OCH}_2\text{OCH}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{OCHOCH}_3 + \text{H}_2\text{O}_2$	2.00×10^{12}	0.00	15296	[13]
15	$\text{CH}_3\text{OCH}_2\text{OCH}_2 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{CH}_3\text{OCHO} + \text{OH}$	2.50×10^{11}	0.00	-1700	[22]
16	$\text{CH}_3\text{OCHOCH}_3 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{CH}_3\text{OCHO} + \text{OH}$	2.50×10^{11}	0.00	-1700	[22]
17	$\text{CH}_3\text{OCH}_2\text{OCH}_2 + \text{HO}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{CH}_3\text{OCH}_2\text{O} + \text{OH}$	3.00×10^{11}	0.00	0	[13]
18	$\text{CH}_3\text{OCHOCH}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{OCHO} + \text{CH}_3\text{O} + \text{OH}$	1.00×10^{12}	0.00	0	[13]
19	$\text{CH}_3\text{OCH}_2\text{OCH}_2 + \text{O}_2 \rightleftharpoons \text{CH}_3\text{OCH}_2\text{O}_2 + \text{CH}_2\text{O}$	6.40×10^{12}	0.00	91	see text
20	$\text{CH}_3\text{OCH}_2\text{OCH}_2 + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{OCH}_2\text{O}_2 + \text{CH}_2\text{OH}$	1.00×10^{12}	0.00	0	see text

A in units of cm^3 , mol, s; E_a in cal/mol

Table 3.

Linear sensitivity coefficients for CO for sets 1-9 in Table 1. The sensitivity coefficients are given as $A_i \delta Y_j / Y_j \delta A_i$, where A_i is the pre-exponential constant for reaction i and Y_j is the mass fraction of j_{th} species. Therefore, the sensitivity coefficients listed can be interpreted as the relative change in predicted concentration for the species j caused by increasing the rate constant for reaction i by a factor of 2.

Reaction	set 1 (623 K)	set 2 (623 K)	set 3 (573 K)	set 4 (673 K)	set 5 (623 K)	set 6 (523 K)	set 7 (548 K)	set 8 (548 K)	set 9 (548 K)
(9) CH ₃ OCH ₂ OCH ₃ +OH=CH ₃ OCH ₂ OCH ₂ +H ₂ O	1.019	0.958	0.989	1.303	0.974	1.160	1.397	1.350	1.303
(10) CH ₃ OCH ₂ OCH ₃ +OH=CH ₃ OCHOCH ₃ +H ₂ O	-0.219	-0.230	-0.352	-0.479	-0.251	-0.392	-0.487	-0.485	-0.479
(11) CH ₃ OCH ₂ OCH ₃ +HO ₂ =CH ₃ OCH ₂ OCH ₂ +H ₂ O ₂	0.112	0.126	0.025	0.025	0.097	0.046	0.022	0.025	0.025
(12) CH ₃ OCH ₂ OCH ₃ +HO ₂ =CH ₃ OCHOCH ₃ +H ₂ O ₂	0.126	0.124	0.022	0.033	0.087	0.086	0.035	0.036	0.033
(14) CH ₃ OCH ₂ OCH ₃ +O ₂ =CH ₃ OCHOCH ₃ +HO ₂	-	-	0.001	0.001	-	0.017	0.007	0.003	0.001
(16) CH ₃ OCH ₂ OCH ₂ +O ₂ =CH ₂ O+CH ₃ OCHO+OH	-0.184	-0.177	-0.216	-0.302	-0.182	-0.280	-0.322	-0.312	-0.302
(19) CH ₃ OCH ₂ OCH ₂ +O ₂ (+M)=CH ₃ OCH ₂ O ₂ +CH ₂ O(+M)	0.179	0.174	0.214	0.301	0.179	0.279	0.317	0.309	0.301
CH ₃ OCH ₂ +O ₂ =CH ₂ O+CH ₂ O+OH	-0.021	-0.017	-0.008	-0.001	-0.017	-0.002	-0.001	-0.001	-0.001
CH ₂ OCH ₂ O ₂ H=CH ₂ O+CH ₂ O+OH	-1.479	-1.223	-0.705	-0.024	-1.164	-0.167	-0.075	-0.037	-0.024
CH ₃ OCH ₂ O ₂ =CH ₂ OCH ₂ O ₂ H	0.001	0.001	0.001	0.006	0.001	0.016	0.017	0.009	0.006
O ₂ CH ₂ OCH ₂ O ₂ H=CH ₂ OCH ₂ O ₂ H+O ₂	1.503	1.242	0.725	0.028	1.183	0.296	0.107	0.045	0.028
HO ₂ CH ₂ OCHO=OCH ₂ OCHO+OH	-0.028	-0.008	0.559	1.468	-0.006	1.659	1.795	1.614	1.468
CH ₃ OCHO+OH=CH ₂ OCHO+H ₂ O	0.071	0.059	0.023	-0.031	0.061	-0.054	-0.057	-0.044	-0.031
CH ₃ OCHO+OH=CH ₃ OCO+H ₂ O	0.002	0.004	-0.011	-0.021	0.004	-0.017	-0.023	-0.022	-0.021
CH ₂ OCHO+HO ₂ =HO ₂ CH ₂ OCHO	0.011	0.017	0.007	-0.010	0.017	-0.002	-0.007	-0.009	-0.010
H+O ₂ +N ₂ =HO ₂ +N ₂	-0.014	-0.010	-0.001	0.000	-0.005	0.000	0.000	0.000	0.000
OH+HO ₂ =H ₂ O+O ₂	-0.006	-0.005	-0.001	-0.002	-0.005	-0.002	-0.006	-0.003	-0.002
HO ₂ +HO ₂ =H ₂ O ₂ +O ₂	-0.160	-0.234	-0.056	-0.039	-0.192	-0.063	-0.026	-0.036	-0.039
H ₂ O ₂ +M=OH+OH+M	0.091	0.310	0.008	0.001	0.291	0.000	0.000	0.001	0.001
H ₂ O ₂ +OH=H ₂ O+HO ₂	-0.012	-0.030	-0.027	-0.025	-0.037	-0.002	-0.008	-0.017	-0.025
CH ₂ O+OH=HCO+H ₂ O	-0.851	-0.749	-0.608	-0.732	-0.735	-0.692	-0.811	-0.771	-0.732
CH ₂ O+HO ₂ =HCO+H ₂ O ₂	0.094	0.231	0.063	0.037	0.209	0.013	0.013	0.027	0.037
HCO+M=H+CO+M	0.014	0.009	0.003	0.000	0.004	0.001	0.000	0.000	0.000
HCO+O ₂ =HO ₂ +CO	-0.016	-0.012	0.095	0.001	-0.007	0.255	0.006	0.003	0.001

Figure captions

Fig. 1. Influence of pressure on the DMM, CO₂, CO, CH₂O, CH₃OCHO and CH₄ concentration profiles as a function of temperature for a given air excess ratio ($\lambda=0.7$). Sets 1-3 in Table 1.

Fig. 2. Influence of pressure on the DMM, CO₂, CO, CH₂O, CH₃OCHO and CH₄ concentration profiles as a function of temperature for a given air excess ratio ($\lambda=1$). Sets 4-6 in Table 1.

Fig. 3. Reaction path diagram for DMM oxidation according to the current kinetic model in the 373-1073 K temperature range. Solid lines represent the main reaction pathways for all the conditions considered in the present work. Dashed lines refer to reaction paths that become more relevant under oxidizing conditions ($\lambda=20$) and increasing pressure.

Fig. 4. Influence of pressure on the DMM, CO₂, CO, CH₂O and CH₃OCHO concentration profiles as a function of temperature for a given air excess ratio ($\lambda=20$). Sets 7-9 in Table 1.

Fig. 5. Results for stoichiometric conditions, at 1 bar (experimental) from Marrodán et al. [15] and at high-pressure (experimental and modeling) from the present work [pw], sets 4-6 in Table 1.

Fig. 6. Comparison (for DMM, CO and CO₂ concentrations) between modeling calculations obtained with the initial mechanism [15] and the mechanism used in the present work for the experimental results obtained at atmospheric pressure and $\lambda=1$, for the conditions indicated in [15].

Fig. 7. Evaluation through model calculations of the effect of gas residence time (comparison between solid lines, $t_r(s)=5220/T(K)$, and short-dashed lines, $t_r(s)=261/T(K)$) and pressure (comparison between solid lines, $t_r(s)=5220/T(K)$, and long-dashed lines, $t_r(s)=5220/T(K)$) for a selected example under the conditions indicated in set 4, Table 1.

Figures

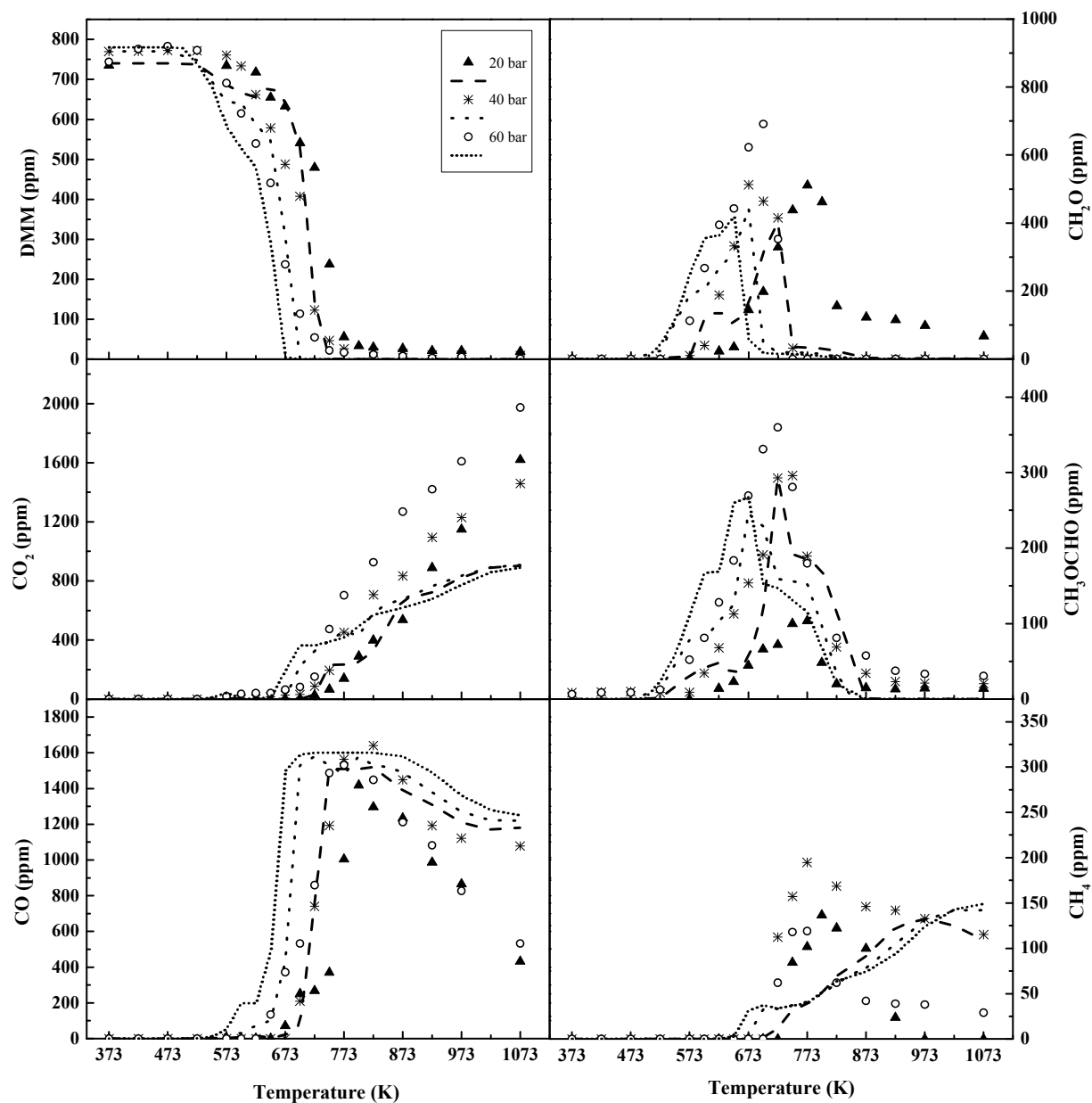


Fig. 1. Influence of pressure on the DMM, CO₂, CO, CH₂O, CH₃OCHO and CH₄ concentration profiles as a function of temperature for a given air excess ratio ($\lambda=0.7$). Sets 1-3 in Table 1.

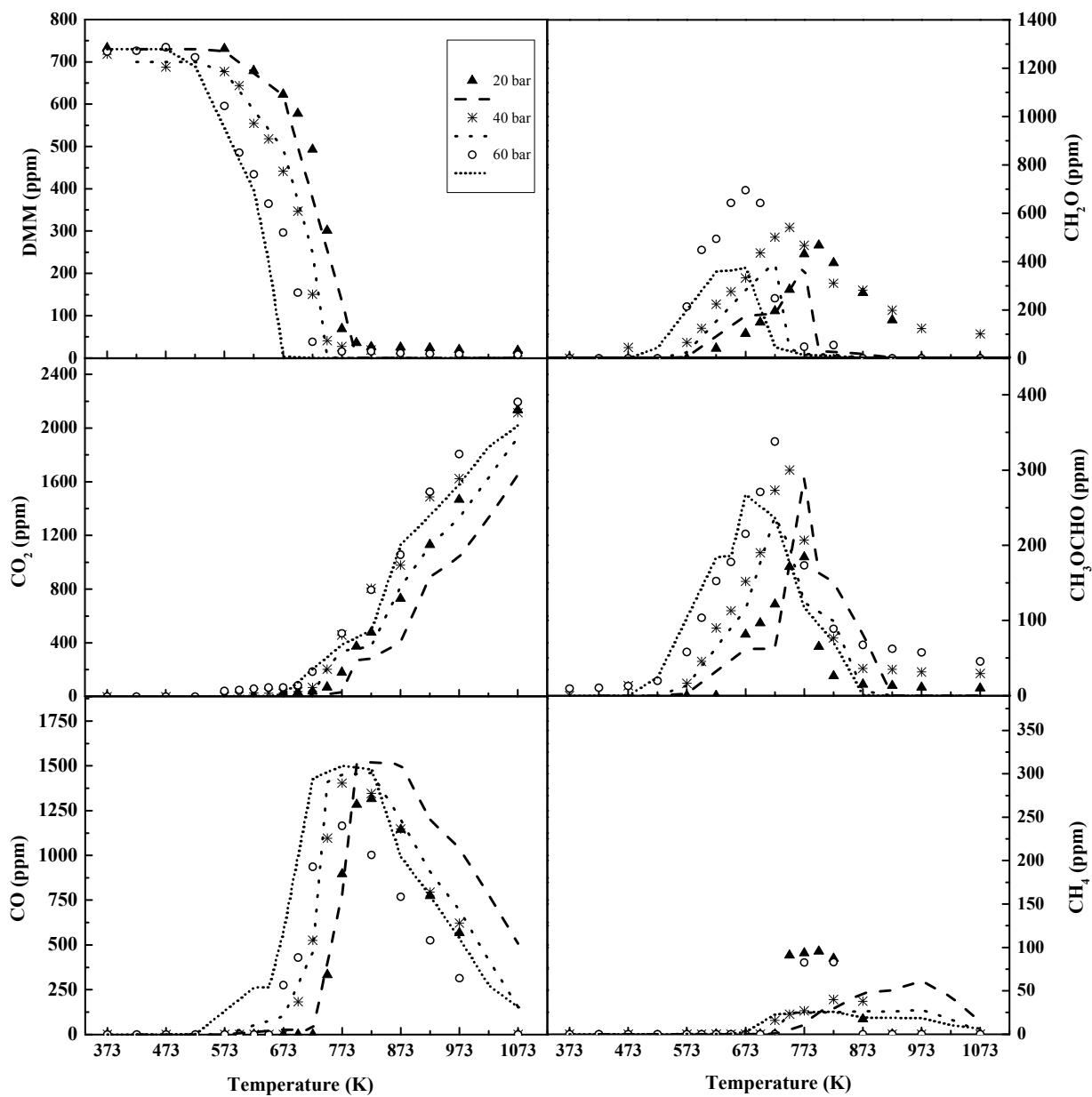


Fig. 2. Influence of pressure on the DMM, CO₂, CO, CH₂O, CH₃OCHO and CH₄ concentration profiles as a function of temperature for a given air excess ratio ($\lambda=1$). Sets 4-6 in Table 1.

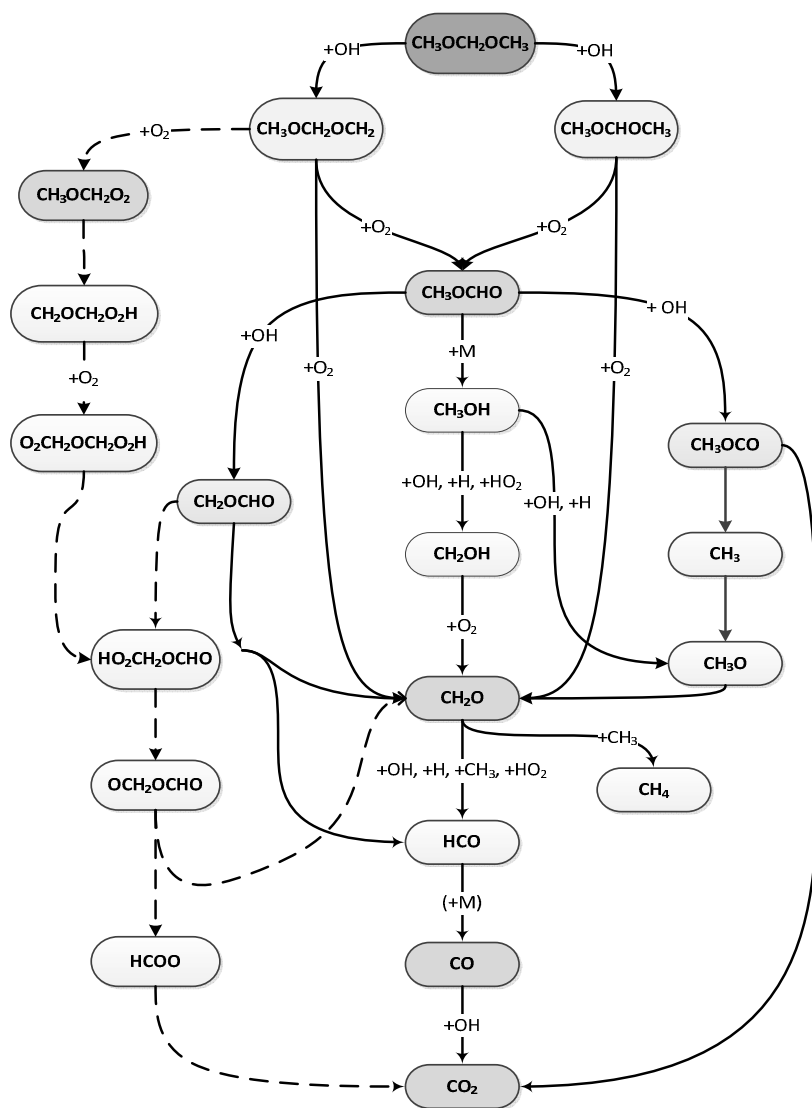


Fig. 3. Reaction path diagram for DMM oxidation according to the current kinetic model in the 373-1073 K temperature range. Solid lines represent the main reaction pathways for all the conditions considered in the present work. Dashed lines refer to reaction paths that become more relevant under oxidizing conditions ($\lambda=20$) and increasing pressure.

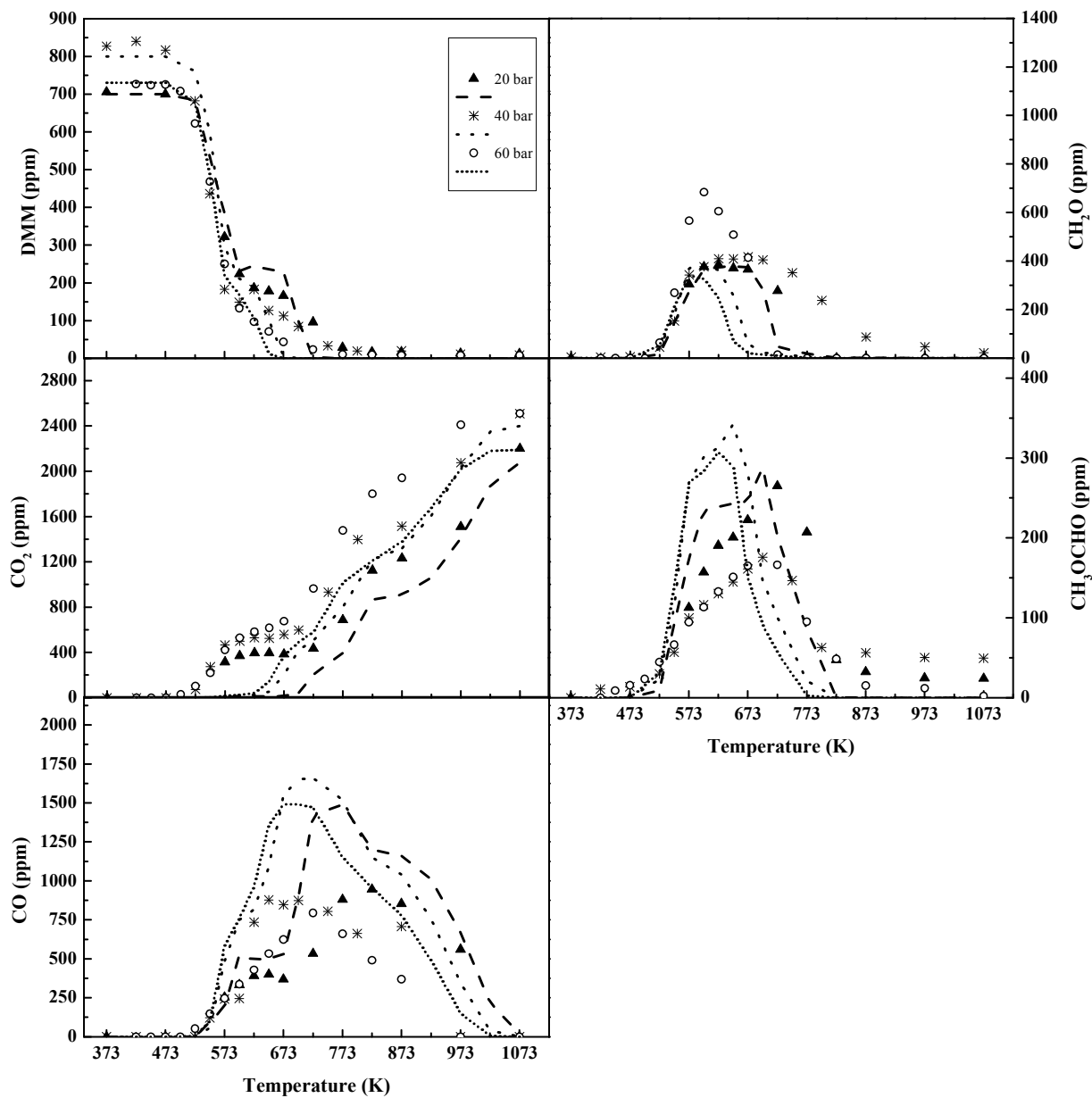


Fig. 4. Influence of pressure on the DMM, CO₂, CO, CH₂O and CH₃OCHO concentration profiles as a function of temperature for a given air excess ratio ($\lambda=20$). Sets 7-9 in Table 1.

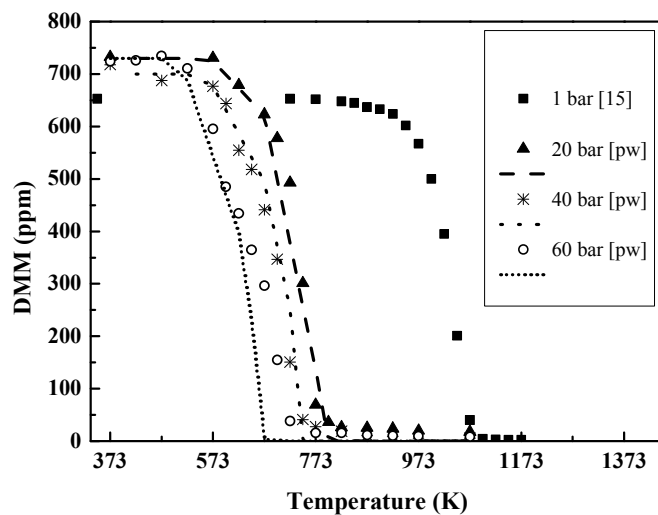


Fig. 5. Results for stoichiometric conditions, at 1 bar (experimental) from Marrodán et al. [15] and at high-pressure (experimental and modeling) from the present work [pw], sets 4-6 in Table 1.

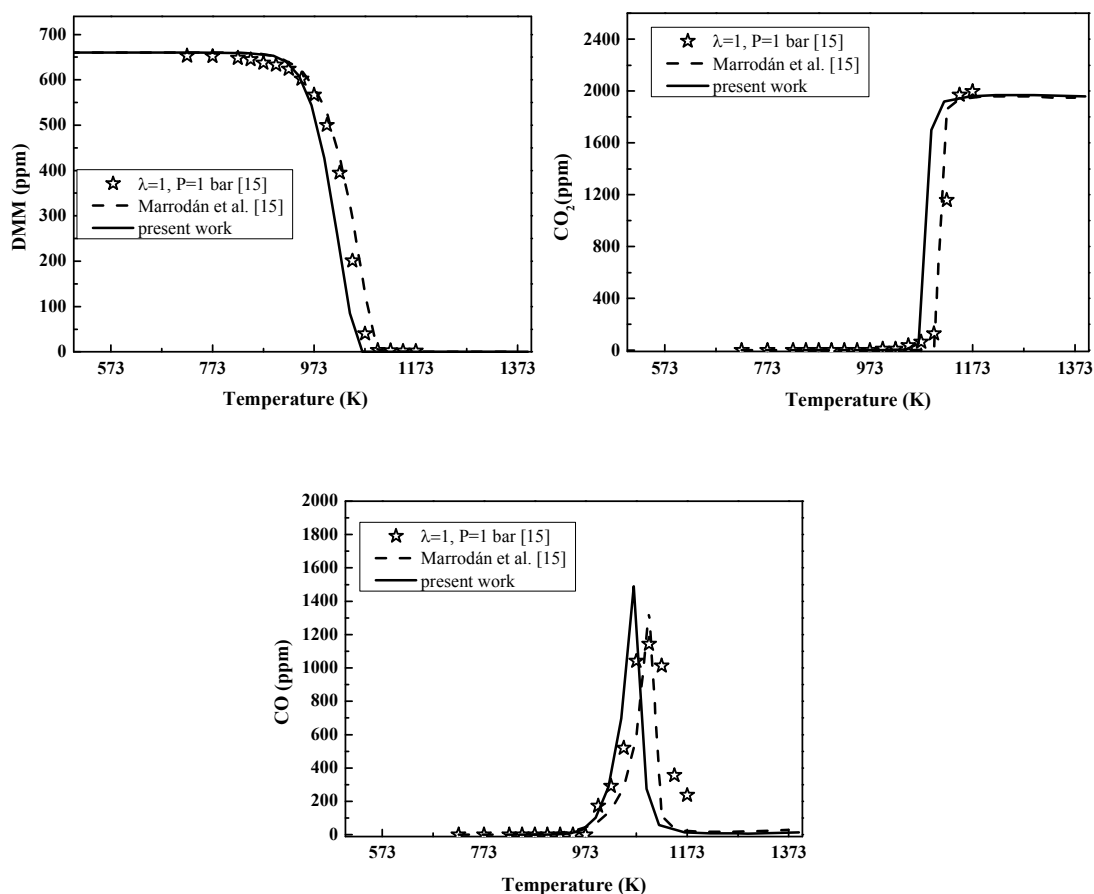


Fig. 6. Comparison (for DMM, CO and CO₂ concentrations) between modeling calculations obtained with the initial mechanism [15] and the mechanism used in the present work for the experimental results obtained at atmospheric pressure and $\lambda=1$, for the conditions indicated in [15].

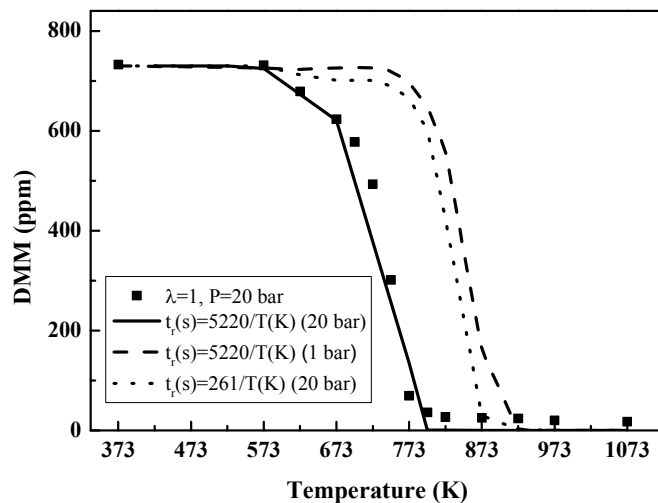


Fig. 7. Evaluation through model calculations of the effect of gas residence time (comparison between solid lines, $t_r(s)=5220/T(K)$, and short-dashed lines, $t_r(s)=261/T(K)$) and pressure (comparison between solid lines, $t_r(s)=5220/T(K)$, and long-dashed lines, $t_r(s)=5220/T(K)$) for a selected example under the conditions indicated in set 4, Table 1.