A study of dimethyl carbonate conversion and its impact to minimize soot and NO emissions

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Abstract

Fuel reformulation through the use of oxygenated compounds has been considered as an interesting option both, to reduce the harmful soot emissions and to overcome the dependence on fossil fuels, since many of them are bio-derived fuels. Dimethyl carbonate (DMC) is of interest as oxygenated fuel additive since it presents a relative high oxygen content as compared with other additives and suitable characteristics to be used in combustion systems. The present work includes the analysis of different fundamental aspects of the DMC combustion process: its oxidation behavior (through experimental and computational analysis), its tendency to produce soot and the role of the NO presence in the reaction system. Experiments are performed under well controlled conditions using specifically designed flow reactor systems. Results obtained contribute to extend the available experimental database on DMC, and show the low tendency of DMC to form soot compared to other oxygenates and its capacity to contribute to NO reduction under specific fuel-rich conditions. Modeling calculations are able to reproduce reasonably well the experimental trends observed, and highlight the sensitivity of the results to the thermodynamic data of DMC and DMC derived species.

Keywords: DMC; Soot; NO; Oxygenated additives; Combustion

1. Introduction

In the line of replacing or minimizing the use of fossil fuels, different alternative fuels such as biofuels are of increasing interest in the research community. Particularly, oxygenated compounds, that can be obtained in biorefinery processes, either used directly as fuel or as additives to diesel fuels, can be appropriate to reduce the emissions of soot in diesel engines.

Ren et al. [1] analyzed the influence of blending different oxygenated compounds (esters, ethers and alcohols) with diesel on the combustion and emissions of a diesel engine. The authors observed that,

regardless of the kind of oxygenate additive, soot emissions were decreased, in particular, with the increase of the oxygen mass fraction in the blends, without increasing the NO_x emissions and without reducing engine thermal efficiency. Hydrocarbons (HC) concentrations also decreased with the increase of oxygen mass fraction in the blends. Westbrook et al. [2] conducted a chemical kinetic modeling study of the effects of oxygenated compounds with different functional group on soot emissions from diesel engines, and observed that for the same mass fraction of oxygen, esters were less effective than ethers or alcohols. In this research line, Pepiot-Desjardins et al. [3] analyzed the influence of the functional group for soot reduction tendency of oxygenated fuels. They highlighted two main factors that can decrease the tendency to form soot precursors: the oxygen content in the molecule and the dilution effect due to the replacement of part of the fuel by less sooting precursor compounds. Other important properties of fuel additives listed by McEnally and Pfefferle [4] to reduce soot are: a small number of carbon atoms in their structure, the presence of interspersed oxygen atoms within the carbon chain and the absence of ramifications. In addition, to obtain a good performance of the fuel-oxygenated additive blend, the cetane number should be around 50–60 and the oxygen weight content in the blend between 10% and 20% [5].

Considering these characteristics, dimethyl carbonate (DMC), $CH_3OCOOCH_3$, has been suggested as a promising oxygenated additive to diesel fuels due to its high oxygen content [6,7], the absence of carbon–carbon atomic bonds, suitable boiling point and solubility in diesel fuel [7]. DMC has been also considered as an option for replacing methyl tertiary butyl ether (MTBE) in commercial gasoline to meet with Clean Air Act specification for oxygen in gasoline [8]. In addition to its good properties as an additive to diesel fuels, DMC can be synthesized by transesterification of cyclic carbonates with methanol; and these two components can be obtained from biorefinery processes [9,10]. Preliminary results on the use of DMC as a fuel additive in a diesel engine, equipped with exhaust gas recirculation, suggest that both lower soot and NO_x emissions can occur [e.g. 11]; however, the relative importance of using DMC as an additive on these emissions is unknown. Under laboratory scale conditions, Chen et al. [12] investigated the effect of different oxygenated compounds, including DMC, on laminar premixed low pressure (30 Torr) n-heptane flames. The authors observed an early formation of CO_2 in the DMC-doped flame, which was attributed to the decomposition of DMC and its subsequent intermediates. They also concluded that the C_1–C_5 hydrocarbon intermediates and benzene concentrations decreased when any of the oxygenated compounds were added to the n-heptane flame.

Although there is evidence that it is possible to add fractions of DMC to both gasoline and diesel fuels maintaining a good engine performance [8], laboratory scale studies regarding this compound are very limited despite the importance of these studies to characterize the reaction scheme involving its conversion process. Therefore, there is a clear need to develop further studies to understand how the oxidation of this compound occurs and to investigate its contribution to the minimization of pollutant emissions.

In 1997, Bilde et al. [13] investigated the atmospheric chemistry of DMC in the 252–370 K temperature range by using flash photolysis-resonance fluorescence techniques, to address the environmental impact of DMC in the case that it is released into the atmosphere. The authors concluded that, under these conditions, the reactivity of DMC toward OH radicals is low and is comparable to that of ethane. Subsequently, Sinha and Thomson [14] performed an experimental study of the oxidation of DMC in a diffusion flame, at atmospheric pressure and in the 200–2000 K temperature range. They outlined that the conversion of DMC produces very low levels of methane, ethane, ethylene, and acetylene, due to the presence of oxygen on the central carbon in DMC that favors the breakage of the O–CO bond, forming methoxy radical. The experimental results from this study were further used to develop a chemical kinetic mechanism for DMC oxidation [6]. In this way, Glaude et al. [6] proposed a reaction mechanism for the oxidation of DMC and used it to kinetically analyze its combustion in an opposed flow diffusion flame. They identified the reactions with H and OH radicals as the main consumption paths of DMC.

Recently, Hu et al. [15] have published an experimental and kinetic modeling study on ignition delay times, in the 1100–1600 K temperature range, for equivalence ratios in the range $\phi=0.5$–2.0. Their results indicate that the DMC is mainly consumed through H abstraction and that unimolecular decomposition is not relevant under their conditions.

To our knowledge, up to date, these are the only studies that address the conversion process of DMC under well-characterized laboratory conditions. All of them have been focused on the conversion of DMC, both experimental and kinetic modeling points of view, but so far the studies have not concentrated on the formation of pollutant emissions. Therefore, the present study on the conversion of DMC over a wide range of operating conditions, and in the presence of NO, provides necessary experimental data, both to get insight into the phenomena controlling the process and to improve and update a gas-phase combustion scheme applicable in different reaction environments. In particular, emphasizing the impact of DMC addition on the emissions of pollutants, specifically on soot formation and NO reduction.

Table 1
Experimental conditions.

Set	Environment	λ	t_r (s)	[DMC] ppm	[O_2] ppm	[H_2O] ppm	[NO] ppm
1[*]	Pyrolysis	0	3.09	50,000	0	0	0
2	Fuel-rich	0.3	195/T(K)	300	300	7000	500
3	Fuel-rich	0.3	195/T(K)	300	300	7000	0
4	Fuel-rich	0.7	195/T(K)	300	630	7000	500
5	Fuel-rich	0.7	195/T(K)	300	630	7000	0
6	Stoichiometric	1	195/T(K)	300	900	7000	500
7	Stoichiometric	1	195/T(K)	300	900	7000	0
8	Fuel-lean	35	195/T(K)	300	31,500	7000	500
9	Fuel-lean	35	195/T(K)	300	31,500	7000	0

[*] See text for details of the reaction system and experimental procedure of experiment 1.

2. Experimental

The experimental installation was specifically designed to obtain data for performing gas-phase chemical-kinetic analysis of the conversion process of gaseous fuels (i.e. hydrocarbons, alcohols, etc.) in different reaction environments. It has been used with success in many previous studies by the group [e.g. 16,17]. The detailed description of the installation can be found elsewhere [18], and therefore only a brief description is given here.

The reaction takes place in a quartz plug-flow reactor, according to the design of Kristensen et al. [19], which is placed in a three-zone electrically heated oven to ensure a uniform temperature profile within ±5 K throughout the reaction zone. The reaction zone has 8.7 mm inside diameter and 200 mm in length. Gases (DMC, O_2, NO and N_2) are supplied from gas cylinders through mass flow controllers and H_2O is fed by saturating a nitrogen stream through a bubbling water system at room temperature; water is added because it is present in most combustion real systems and to minimize the effect of radical recombination in the reactor walls. These gases are supplied in up to four separate streams and mixed just prior to entering the reaction zone. The configuration of the injection system has been designed following the investigations of Alzueta et al. [20].

Experiments of DMC conversion in the absence and presence of NO were carried out at atmospheric pressure, in the 700–1400 K temperature range, and with a total flow rate of 1000 mL (STP)/min using N_2 to balance. Considering the volume of the reaction zone and the constant STP flow rate, the residence time of the gases is only function of the reaction temperature in the way of: t_r (s) $=195/T(K)$. The stoichiometry of the reaction (λ) is defined as the quotient between the O_2/DMC ratio available for reaction and the stoichiometric O_2/DMC ratio, covering conditions from very fuel-rich ($\lambda=0.3$) to very fuel-lean ($\lambda=35$). Table 1 summarizes the experimental conditions tested.

At the outlet of the reaction zone, the reactor has a cooling jacket. Thus, the product gas is efficiently quenched, by means of external refrigeration with cooling air. The product gas composition has been quantified by continuous CO, CO_2 and NO IR analyzers and a gas chromatograph equipped with TCD detector for quantifying hydrocarbons and oxygenated compounds. The main gases quantified in this study are: DMC, CO, CO_2 and NO (when present), but, depending on the specific operating conditions, also minor concentrations of C_2H_4 and C_2H_6 where obtained. The estimated uncertainties in the measurements are $\pm5\%$ for both, the continuous IR analyzers and the gas chromatograph, but not less than 10 ppm. Repeated experiments on different, not consecutive, days, showed a good agreement in most of the data points compared (see Fig. 3). The carbon balance was checked for each condition and temperature studied and was found to close in general as $95\pm10\%$.

Experiment 1 has been carried out in a different reaction system, which was specifically designed to analyze the formation of soot from different fuels (e.g. [21]). This system is constituted by a quartz flow reactor with a reaction zone of 45 mm inside diameter and 160 mm in length placed into a one-zone electrically heated oven, and a soot collection system that includes a quartz fiber filter of 25 mm diameter and 60 mm in length, with a mesh size lower than 1 µm. In this experiment, the reaction system was heated up to 1475 K in a N_2 atmosphere before feeding the reactant DMC–N_2 mixture and, to supply the desired DMC concentration to the reactor (50,000 ppm), pure liquid DMC was pumped through the use of an isocratic HPLC pump, subsequently vaporized in a thermally insulated line and mixed with the nitrogen. Afterwards, the DMC–N_2 mixture was fed into the reaction system (total flow rate of 1000 mL (STP)/min), considering this moment as the initial time for the experiment. The experiment last was 3 h and, during this time, the soot formed was collected for its subsequent quantification, and

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Table 2
Yields to soot (η_{soot}) from different compounds and mixtures. 50,000 ppm of reactants and N_2 to balance, residence time: 3.09 s.

Mixture	DMC	C_2H_2	C_2H_5OH	$C_2H_2+10\%C_2H_5OH$	$C_2H_2 +20\%C_2H_5OH$	$C_2H_2 +40\%C_2H_5OH$
O/C (molar)	1	-	0.5	0.05	0.1	0.2
η_{soot}(%)	10.2	58	28.7	45	39	37
Ref.	P.w.*	[21]	[29]	[28]	[28]	[28]

* P.w.: present work.

the product gas composition was analyzed by gas chromatography.

3. Modeling

Simulation of the experimental results has been made using a gas-phase chemical kinetic modeling for DMC oxidation process and the Senkin [22], the plug-flow reactor code from the CHEMKIN [23] kinetic-chemical package. The reaction mechanism used is taken from previous works by the authors, described and updated so far [i.e. 16,24–27], with the subsequent implementation without modification of the DMC oxidation subset given by Glaude et al. [6]. The full listed mechanism can be found as supplemental material (SMM-1). In general, the thermodynamic data are taken from the same sources as the original mechanisms. However, as it will be seen further below, calculation results have been found to be very sensitive to the thermodynamic data of the DMC subset. Therefore, this aspect will be analyzed and further discussed in the text, and the present limitations to properly simulate DMC conversion are identified.

4. Results and discussion

As a first step to evaluate the possible use of DMC as a fuel additive to minimize soot emissions, it is important to assess its tendency to form soot. DMC has no C–C bonds in its structure and has a molar O/C ratio of 1, which, in principle, are positive characteristics to generate a minimum amount of soot. 50,000 ppm of DMC in nitrogen were pyrolyzed at a temperature of 1473 K in a flow reactor (experiment 1 in Table 1). The amount of soot collected was 1.49±10% g, which represents a yield to soot of 10.2%, defined as the percentage of the carbon present in soot compared to the carbon present in the fed gases. Apart from soot, the main gases collected showed the following concentrations: 1169 ppm DMC, 71,338 ppm H_2, 69,173 ppm CO, 10,631 ppm CO_2, 564 ppm C_2H_4, 2464 ppm C_2H_2, 150 ppm C_6H_6, and 6862 ppm CH_4.

In order to assess the tendency to form soot by DMC, it is interesting to compare the results of soot formation from DMC and those obtained
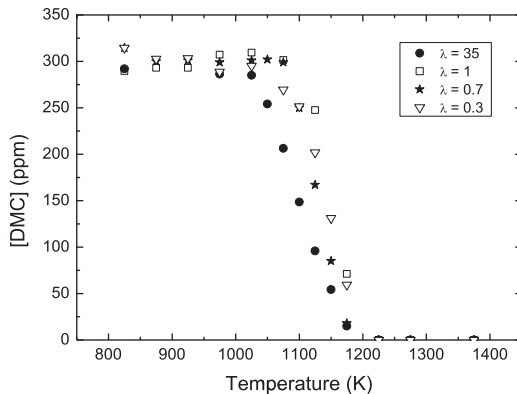

Fig. 1. Conversion of DMC as a function of temperature for different stoichiometries. Inlet conditions correspond to sets 3, 5, 7 and 9 in Table 1.

under similar experimental conditions with other compounds. Thus, Table 2 shows the yields to soot obtained in the present work, together with literature data on the yield to soot of acetylene (as a well-known soot precursor), ethanol (probably the most studied fuel as additive), and acetylene–ethanol mixtures. The yield to soot obtained in the pyrolysis of DMC is significantly lower compared to the soot obtained in the pyrolysis of ethanol and much lower than in the acetylene case, or in the pyrolysis of the acetylene–ethanol mixtures. This indicates that DMC can be a good candidate as fuel additive in relation to soot minimization.

In order to further study the conversion of DMC under well-controlled laboratory conditions, experimental results on DMC conversion and CO and CO_2 formation as function of temperature and for different stoichiometries are shown in Figs. 1 and 2.

As shown in Fig. 1, for fuel-rich (λ =0.3 and 0.7) and stoichiometric (λ =1) conditions, the conversion profile of DMC is not significantly influenced by the oxygen concentration in the reaction environment. Neither the initiation temperature nor the temperature window for the DMC consumption are appreciably modified under these conditions. DMC starts reacting at around 1100 K up to be fully consumed at 1200 K. Only for very fuel-lean conditions (λ =35), the initial temperature for DMC consumption is shifted 50 K to lower
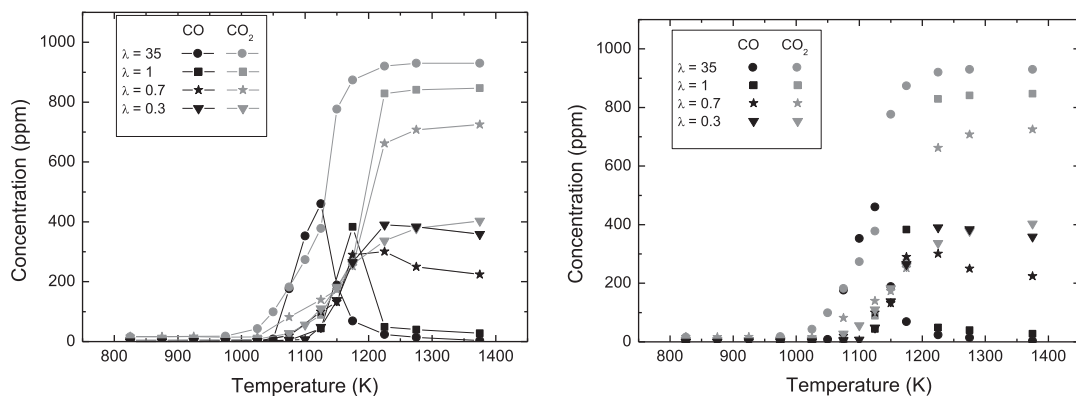
Fig. 2. Experimental evolution of CO and CO_2 from the oxidation of DMC as a function of temperature for different stoichiometries. Inlet conditions correspond to sets 3, 5, 7 and 9 in Table 1.

temperatures, indicating a promotion of the DMC conversion presumably originated by the enhanced oxidation process. The same trend is observed in the formation of CO and CO_2 with temperature (Fig. 2). However, in this case, the specific concentration profiles are influenced by the stoichiometry. The CO concentration shows a maximum for all the conditions studied, but in general at lower temperatures and of higher magnitude as the oxygen concentration is increased. The formation of CO_2 is also enhanced by higher oxygen concentrations.

In order to assess the interaction between DMC and NO, Figs. 3 and 4 show respectively the experimental results of DMC conversion in the absence and presence of 500 ppm of NO, and the concentration of NO as a function of temperature.

As seen in Fig. 3, the presence of NO does not modify significantly the conversion of DMC under fuel-rich and stoichiometric conditions, while NO promotes the conversion of DMC under very fuel-lean conditions, shifting its conversion profile 200 K towards lower temperatures. This behavior is related to the NO concentration results of Fig. 4, in which the NO–NO_2 interconversion acts to replenish the O/H radical pool, which is responsible for the sensitized oxidation of DMC, as it has been described for a number of fuels (e.g. [30]). For high temperatures and stoichiometric or fuel-rich conditions, the concentration of NO decreases, indicating that under these conditions reburn reactions act to diminish the concentration of NO [20]. Thus, in the presence of typical pollutants present in an engine chamber, such as NO, DMC appears to exhibit a positive behavior. Under fuel-lean conditions, the presence of NO contributes to favor DMC conversion and thus possibly minimizes the formation of soot, because, considering the sensitized oxidation of DMC, any intermediate product originated from DMC conversion will have more time to react. Under fuel-rich conditions, reaction pathway analysis indicates that DMC generates hydrocarbon radi-
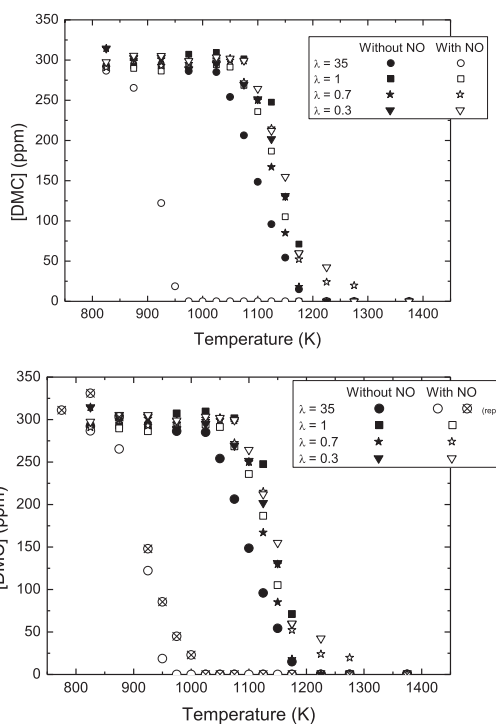

Fig. 3. Influence of the NO presence on the conversion of DMC as a function of temperature and for different stoichiometries. Inlet conditions correspond to sets 2-9 in Table 1. Results of repeated experiments in set 9 (Table 1) conditions are included.

cals able to participate in reburn reactions, and thus can act to remove both NO and the carbon compounds from the typical pathways that lead to soot formation [27].

In order to get some more insight of the present results, kinetic modeling of DMC conversion may
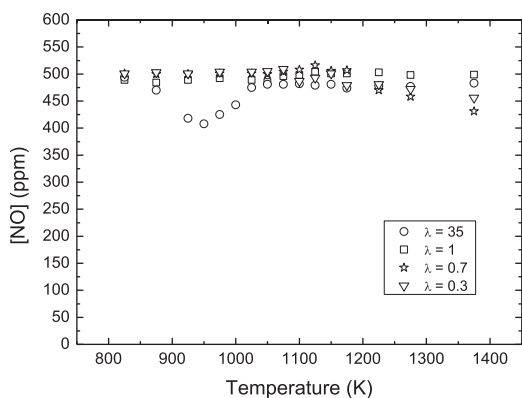
Fig. 4. Conversion of NO during the oxidation of the DMC–NO mixtures, as a function of temperature for different stoichiometries. Inlet conditions correspond to sets 2, 4, 6 and 8 in Table 1.

be helpful. As it has been mentioned in the introduction section, not many studies have considered the oxidation of DMC and even less the pyrolysis of this compound, and the subset proposed by Glaude et al. [6] for DMC oxidation, largely based on estimations, has been added to the mechanism developed in our group to simulate the present results. However, the agreement between experiments and calculations is not very good, as seen in Fig. 5 in the comparison of experimental results together with calculations for stoichiometric conditions ($\lambda=1$). Calculations are shifted around 100 K toward higher temperatures compared to experimental results.

Analyzing the sensitivity of the mechanism to the different parameters, both kinetic and thermodynamic, calculations appear to be particularly sensitive to the thermodynamic data involved in the DMC reaction subset. Glaude et al. [6] estimated the thermodynamic parameters of DMC and derivatives using CBS-Q methods, and Glaude estimations may involve uncertainty. In order to evaluate the impact and sensitivity of the results to the thermodynamic data used for the calculations, a new estimation has been made in the present work using the methodology proposed by Ritter and Bozzelli through the use of the THERM [31] software. This software uses the group additivity method to estimate the thermodynamic properties of molecules and their radicals. The rules followed to calculate the corresponding thermodynamic properties are based on the proposals by Benson and Buss [32]. The inlet parameters for the calculations are the type and number of groups in the molecule, the number of rotors and, optionally, the number of symmetries. The default symmetry number given by the software, which is 1, was used for all the molecules studied. The thermodynamic data for the radicals are obtained via its "mother"

molecule, by abstracting an atom, for example a hydrogen, from the desired position in the "mother" molecule.

The thermodynamic data obtained in the present work for the selected species together with the enthalpies of formation given by Glaude et al. [6] are summarized in Table 3. We are aware that the CBS-Q methods are probably more accurate to calculate thermodynamic data. However, the differences compared to Glaude et al. [6] estimations and the sensitivity of model calculations to thermodynamic data found (see discussion below) indicate the importance of being conscious of the impact of thermodynamics and the necessity of more accurate determinations.

Figure 5 also includes the modeling results obtained using the thermodynamic data calculated in this work with the THERM [31] software. As it can be observed, the chemical-kinetic modeling is very sensitive to the thermodynamics involved in the process. When the thermodynamic data taken from the literature are used, the predicted conversion of DMC is shifted toward higher temperatures with respect to the experimental results, whereas the results obtained with the use of the here calculated thermodynamic data show that the conversion of DMC is shifted to lower temperatures when compared with the experimental results. Therefore, it is clear the sensitivity of the DMC conversion process to the specific thermodynamic data of the DMC derived species.

Considering the results obtained, we performed a sensitivity analysis to the thermodynamics of the process to identify the species whose simulation results are more sensitive to. To perform this analysis we have considered the influence of the given formation enthalpy by keeping fixed the rest of thermodynamic parameters. Therefore, considering the results shown in Table 3 and the formation enthalpy values for these species from the literature [6], we have calculated the average enthalpy of formation and observed how the performance of the model is modified when testing each individual species: $CH_3OCOOCH_2$, CH_3OCOO and CH_2OCOOH. This study has not been conducted with CH_3OCOOH, since the difference between the formation enthalpy value proposed in the literature and the one obtained in this study differs in less than 1 kcal/mol, which may lie within the typical uncertainties for enthalpies of formation.

Through this analysis we have identified that the enthalpy of formation of the species CH_3OCOO (MCr) greatly influences the chemical-kinetic modeling of the DMC conversion process, and the results are shown in Fig. 6. For the other species, no influence of the given formation enthalpy value was observed. These results limit the uncertainties to the CH_3OCOO species, for which accurate thermodynamic data are needed.
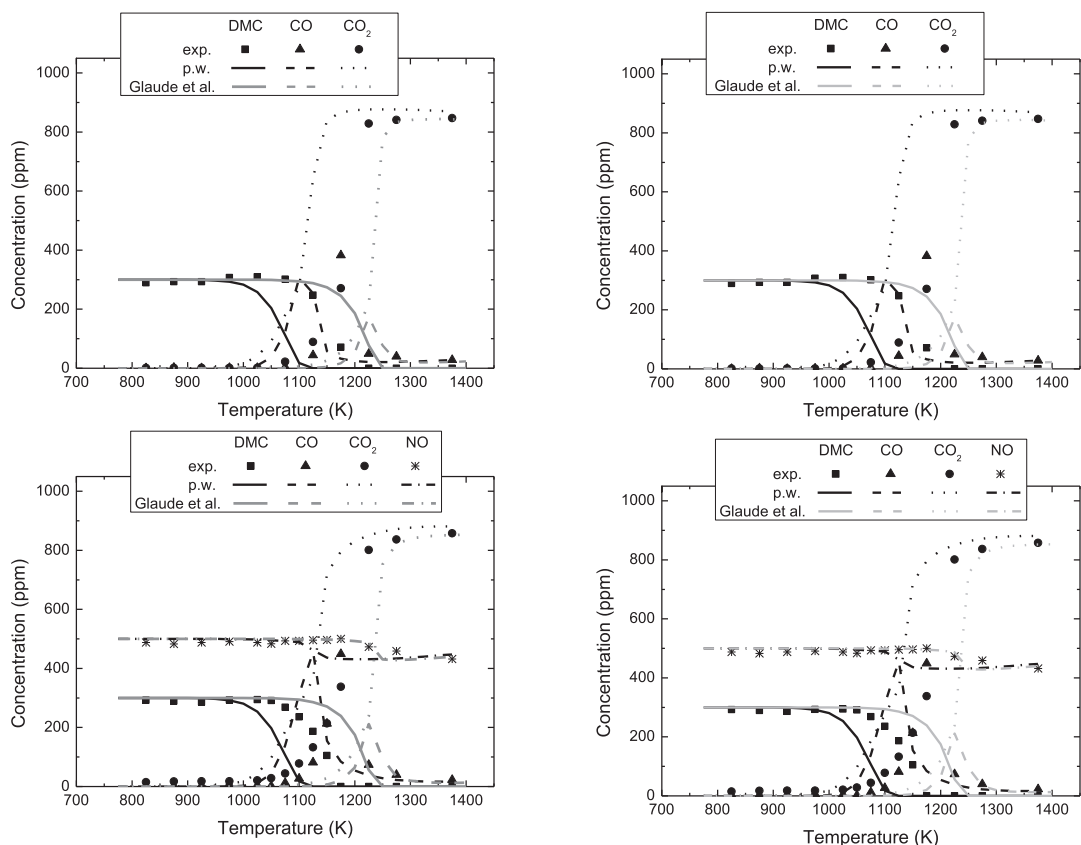
Fig. 5. Comparison of experimental and predicted results of DMC, CO, CO_2 and NO as a function of temperature and for stoichiometric conditions ($\lambda=1$). Lines denote model predictions obtained with the thermodynamics proposed by Glaude et al. [6] (grey lines) and with the thermodynamic data proposed in the present work (black lines). The inlet conditions correspond to sets 5 (upper part) and 6 (bottom part) in Table 1.
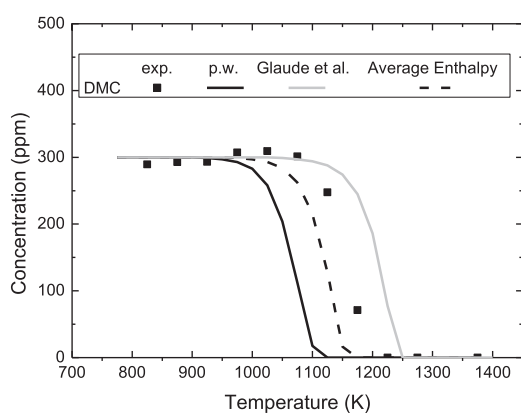

Fig. 6. Comparison of experimental and predicted results of DMC as a function of temperature and stoichiometric conditions ($\lambda=1$). Lines denote model predictions obtained with different values for the enthalpy of formation of CH_3OCOO. The inlet conditions correspond to set 5 in Table 1.

Despite the uncertainty in the thermodynamic parameters and the impact on the temperature window in which conversion of DMC occurs, we have confirmed that the main reaction pathways are not affected by the thermodynamic data. Thus, the present mechanism can be used to determine the main reaction pathways happening during the conversion of DMC. These results are included as supplemental material (SMM-2; Figure S1) together with the sensitivity analysis results (SMM-2; Table 1S). Main outcomes are briefly discussed as follows.

The results of the reaction rate analysis indicate that the initiation reactions involved in the conversion of DMC are not significantly affected by the reaction environment when considering fuel-rich and stoichiometric conditions (Figure S1a). DMC mostly reacts by interaction with H to yield $CH_3OC(=O)OCH_2$, and through its decomposition yielding $CH_3OC(=O)O$ and CH_3 radicals. Sensitivity analysis results also indicate that the process is highly sensitive to these two reactions (Table 1S). These intermediate products, through

Table 3
Calculated thermodynamic data for selected species involved in the oxidation of DMC using the THERM [31] software and enthalpies of formation given by Glaude et al. [6].
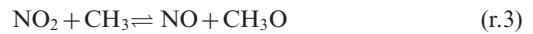
Species*	Glaude et al. [6]	Present work							
	$H^{\circ}_{f\,298\,K}$ (kcal/mol)	$H^{\circ}_{f\,298\,K}$ (kcal/mol)	S (298 K) (cal/mol·K)	Cp(300 K) (cal/mol·K)	Cp(400 K) (cal/mol·K)	Cp(500 K) (cal/mol·K)	Cp(600 K) (cal/mol·K)	Cp(800 K) (cal/mol·K)	Cp(1000 K) (cal/mol·K)
DMCr	−88.10	−91.59	85.40	26.68	30.91	34.58	37.81	43.05	47.21
MC	−140.93	−141.77	74.05	19.86	23.84	27.19	29.94	34.40	37.71
MCr	−82.29	−89.90	74.84	18.55	21.97	24.87	27.25	31.13	33.97
rMC	−93.64	−97.39	75.39	20.38	23.76	26.39	28.49	31.90	34.44

* Correspondence between the nomenclature used and the formula of the species: DMCr ($CH_3OCOOCH_2$); MC (methyl carbonate, CH_3OCOOH); MCr (CH_3OCOO); rMC (CH_2OCOOH).

further reactions, produce finally CO and CO_2. It is worth to note the fact that DMC decomposition yields almost directly CO and CO_2, which can be related to the low tendency of DMC to produce soot since pyrolytic conditions will favor this thermal decomposition reaction route.

For fuel lean conditions, Figure S1b, the initiation reactions of DMC conversion differ from those at fuel richer conditions ($\lambda=1$ and lower). These conditions favor the formation of oxidizing radicals such as O and OH, which, in addition to H radicals, are responsible of most of DMC consumption. The effect of the increased O and OH radical pool makes the reaction path that leads to the formation of $CH_3OC(=O)OCH_2$ to dominate over the DMC decomposition, resulting in nearly one main initiation reaction, which even takes place at lower temperatures.

Reaction path analysis has also been used to identify the main reactions of the DMC–NO system. According to this analysis, the presence of NO provides a new source of OH radicals at low temperature and in the presence of high O_2 concentrations ($\lambda=35$). Under these conditions, NO is converted to NO_2 by transforming the less reactive HO_2 radicals into the more reactive OH radicals (r.1). Subsequently, NO_2 is converted back into NO through reaction r.2, which also favors the production of OH radicals, and reaction r.3.

$$NO + HO_2 \rightleftharpoons NO_2 + OH \qquad (r.1)$$

$$NO_2 + H \rightleftharpoons NO + OH \qquad (r.2)$$

$$NO_2 + CH_3 \rightleftharpoons NO + CH_3O \qquad (r.3)$$

Therefore, the promoted OH radical pool is the responsible of the shift to much lower temperatures of the onset temperature for the consumption of DMC (Fig. 3), coinciding with the temperature window for the NO to NO_2 conversion (Fig. 4). In fact, DMC is mainly consumed by OH radicals via r.4, result also supported by the sensitivity analysis results.

$$CH_3OC(=O)OCH_3 + OH \rightleftharpoons CH_3OC(=O)OCH_2 + H_2O \qquad (r.4)$$
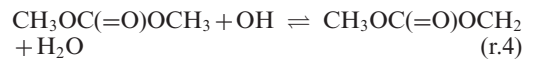
It is worth remarking that the accelerating effect of the NO presence under fuel-lean conditions of DMC conversion is more pronounced than the own effect of the presence of very high O_2 concentrations, indicating the potential of the DMC–NO system, at least under these conditions, for promoting the oxidation of DMC under less favorable conditions (i.e. lower temperatures). Nevertheless, it must also be noticed that the participation of NO in this system does not produce the net removal of NO_x.

At high temperatures (>1175 K) and fuel-rich conditions ($\lambda=0.3$ and 0.7), a reduction of the concentration of NO is observed, which is originated

by reburn reactions, in particular by reactions r.5 and r.6.

$$HCCO + NO \rightleftharpoons HCNO + CO \qquad (r.5)$$
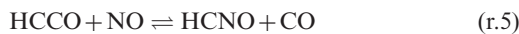
$$HCCO + NO \rightleftharpoons HCN + CO_2 \qquad (r.6)$$

HCCO radicals are formed as intermediate products from the conversion of DMC under both stoichiometric and fuel-rich conditions. However, those radicals are only active in removing NO for fuel-rich conditions. Under stoichiometric conditions, a competition between O_2 attack and NO interaction with hydrocarbon radicals occurs, and an increased oxygen presence (from rich to stoichiometric conditions) causes the HCCO oxidation to be favored compared to its interaction with NO under the specific operating conditions of the present work, as it has also been observed in previous works of the authors [33].

5. Conclusions

A study of DMC conversion at different temperatures and stoichiometries, ranging from pyrolysis to very fuel-lean conditions, has been performed, and the impact of the presence of DMC on soot and NO emissions is evaluated.

The results indicate that DMC contributes to low soot emissions compared, under given conditions, to classical soot precursors such as acetylene, but also compared to other oxygenates used as soot suppressor additives, such as ethanol.

DMC can also contribute to slightly minimize NO emission, because a net reduction of NO_x is found when the DMC–NO interaction occurs at fuel-rich conditions. However, no net reduction of NO_x is found for stoichiometric and fuel-lean conditions. The presence of NO is found to sensitize the conversion of DMC under fuel-lean conditions.

The kinetic mechanism compiled for DMC conversion is able to reproduce reasonably well the experimental trends obtained, and the present study has highlighted the importance of thermodynamic data of DMC and derivatives in the modeling of the process of oxidation of DMC, because the simulation results are very sensitive to them.

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