

Effect of $O_2(a^1\Delta_g)$ on the Low-Temperature Mechanism of CH_4 Oxidation

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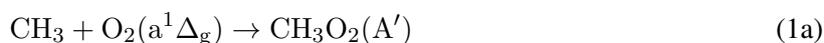
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Singlet Oxygen $O_2(a^1\Delta_g)$ has lately become a subject of intense research [?] because of recent speculations on its capability of significantly enhancing the combustion of hydrocarbons, thus providing opportunities for the elaboration of new combustion-based devices and propulsion systems. Although some efforts were made in modeling methane combustion involving singlet oxygen [1], a reliable theoretical model based on first-principles calculations is required. The most interesting effect of $O_2(a^1\Delta_g)$ is the involvement of this molecule into the reactions of chain initiation and chain propagation. Such an active particle makes the most pronounced impact on the overall kinetics if it is concerned with the enhancement of rate-limiting reactions, which are mostly reactions with chemically stable species, i.e. initiation reactions. Another, and probably more significant option for $O_2(a^1\Delta_g)$, is the enhancement of the process due to participation in chain propagation reactions.

In the first case, $O_2(a^1\Delta_g)$ is mostly consumed by initiation reactions, leading to the multiplication of active radicals and hence, the reduction of the induction time. The second scenario is the enhancement of chain propagation reactions. The potential efficiency of $O_2(a^1\Delta_g)$ is higher for the second scenario, because each excited oxygen molecule could stimulate the production of a greater number of active radicals. At low temperatures, the shift of the reaction equilibrium towards the chain branched mechanism and the acceleration of chain propagation may provide excited oxygen with an additional possibility for enhancing HC combustion. This effect could be achieved using, for example, cold non-equilibrium plasmas [1]. Simulation of this effect requires accurate information about the rates of elementary processes involving $O_2(a^1\Delta_g)$. In fact, an inaccuracy of $5 \frac{\text{kcal}}{\text{mole}}$ in the energetic parameters of a reaction at temperatures below 900 K changes the reaction rate by about one order of magnitude and may become a reason for the incorrect conclusions about the pathways of oxidation in the mechanism.

A kinetic model of methane-air combustion in the presence of $O_2(a^1\Delta_g)$ was proposed in Refs. [1, 2]. This model is focused on the behavior of ignition time and flame velocity at different concentrations of excited oxygen. The kinetic mechanism developed within this model was tested on a rich mixture, high temperatures ($T > 1600\text{K}$), and homogeneous conditions with respect to induction time value and flame velocity. Since the flame velocity is determined by the processes occurring mainly at the flame front [3], there is no strong requirement for the accuracy of the rate characteristics, in contrast to what was mentioned before for low temperatures. Presumably, this is why reactions involving $O_2(a^1\Delta_g)$ are estimated within a rather rough "vibronic terms" model. Nevertheless, this model can be regarded as a basis for the comprehensive theoretical description of combustion process stimulated by $O_2(a^1\Delta_g)$.

One of the key reactions of singlet oxygen in an air-methane mixture is the reaction with the methyl radical.



, which correlate with following channels of reaction of CH_3 with oxygen in the ground state:



Unfortunately, there are no experimental data on the rate parameters of the process 1a. Only several ab initio calculations of this reaction have been performed so far [4, 5]. However, the difference in approaches used for calculations of the Potential Energy Surface (PES) for $\text{CH}_3 + \text{O}_2(\text{a}^1\Delta_g)$ may lead to a contradiction in the conclusions about the input of this reaction to the total oxidation mechanism. The difference in conclusions about the absence [5] or presence [4] of a threshold of the reaction together with the sufficiently great discrepancy for the excitation energies ($26.3 \frac{\text{kcal}}{\text{mole}}$, $24.6 \frac{\text{kcal}}{\text{mole}}$) with respect to the table value ($22.5 \frac{\text{kcal}}{\text{mole}}$) makes the effect of the error propagation of ab-initio calculations upon the final value of the oxidation rate at low temperatures strongly undetermined.

Thus, the accuracy of the models and calculations discussed above is not sufficient for making an unambiguous conclusion about the role of $\text{O}_2(\text{a}^1\Delta_g)$ in methane oxidation at low temperatures. The aim of this study was to find out the principal reactions involving excited oxygen, which provide the maximal sensitivity with respect to the overall kinetic parameters (induction time) and to evaluate the microkinetic characteristics of the key elementary reactions using state-of-the-art computational methods.

The most important processes with $\text{O}_2(\text{a}^1\Delta_g)$ were identified based on a set of simulations with different initial conditions using the Chemical Workbench (CWB) programs package [6]. The autoignition of a mixture $\text{CH}_4:\text{O}_2:\text{N}_2 = 1:2:8$ at a constant atmospheric pressure (Calorimetric Bomb Reactor model) and initial temperature range of 700-2000 K was simulated. The initial chemical composition corresponded to the combustion of a stoichiometric methane-air mixture. The effect of $\text{O}_2(\text{a}^1\Delta_g)$ was simulated by introducing an additional fraction of excited oxygen into the initial mixture. In different simulations the $\text{O}_2(\text{a}^1\Delta_g)$ concentration was varied in the range 0-10% of the initial concentration of $\text{O}_2(\text{X}^3\Sigma_g)$. The enhancement of the process by $\text{O}_2(\text{a}^1\Delta_g)$ was investigated by its influence on the induction time.

Table 1 presents the results of sensitivity analysis for the initial temperature 1000K, atmospheric pressure, initial mixture $\text{CH}_4:\text{O}_2:\text{N}_2 = 1:2:8$, and initial $\frac{[\text{O}_2(\text{a}^1\Delta_g)]}{[\text{O}_2]} = 5\%$. The higher the magnitude of the sensitivity coefficient corresponding to a certain reaction, the greater the impact of a small variation of the corresponding rate parameter to the induction time of the process. Table 1 shows that the reaction 1a corresponds to one of the highest values of sensitivity at the instant close to the ignition moment. From the study of the crucial stages of low-temperature methane oxidation, we can conclude that the reaction 1a is the key one for the reliable kinetic model of the process.

From the study of sensitivity of the crucial stages of low-temperature methane oxidation, the reaction 1a was found to be the key to the reliable description of the process by the kinetic model.

t, s	1e-5	1e-4	1e-3	1e-2	1e-1	$1 \sim t_{ind}$
$\text{HO}_2 + \text{CH}_3 \leftrightarrow \text{OH} + \text{CH}_3\text{O}$	0	0	0.075	1.6	0.55	11.4
$\text{CH}_3 + \text{O}_2(a^1\Delta_g) \rightarrow \text{CH}_3\text{O}_2$	0.055	0.057	0.07	0.54	1.6	7.64
$\text{CH}_3 + \text{O}_2(a^1\Delta_g) \rightarrow \text{CH}_3\text{O} + \text{O}$	0.43	0.61	0.88	1.34	0.01	0.82
$\text{CH}_3 + \text{CH}_3 + \text{M} \leftrightarrow \text{C}_2\text{H}_6 + \text{M}$	0	0	0.02	1.23	0.035	6.63
$\text{CH}_4 + \text{O}_2(a^1\Delta_g) \rightarrow \text{CH}_3 + \text{HO}_2$	1	1	1	0.4	0.013	0.15
$\text{O}_2(a^1\Delta_g) + \text{H} \rightarrow \text{O} + \text{OH}$	0.12	0.15	0.27	1	0.16	0.14
$\text{OH} + \text{CH}_4 \leftrightarrow \text{CH}_3 + \text{H}_2\text{O}$	0.84	1	1	0.95	1.03	1.84
$\text{CH}_2\text{O} + \text{O}_2(a^1\Delta_g) \rightarrow \text{HCO} + \text{HO}_2$	0	0	0	0.53	0.38	2.8

Table 1: Sensitivity coefficients of [OH] to reaction rate parameters at different time moments of the process. $T_{ini}=1000\text{K}$, $P=1\text{ atm.}$, $\text{CH}_4:\text{O}_2:\text{N}_2=1:2:8$ and $\text{O}_2(a^1\Delta_g)=5\%$ O_2

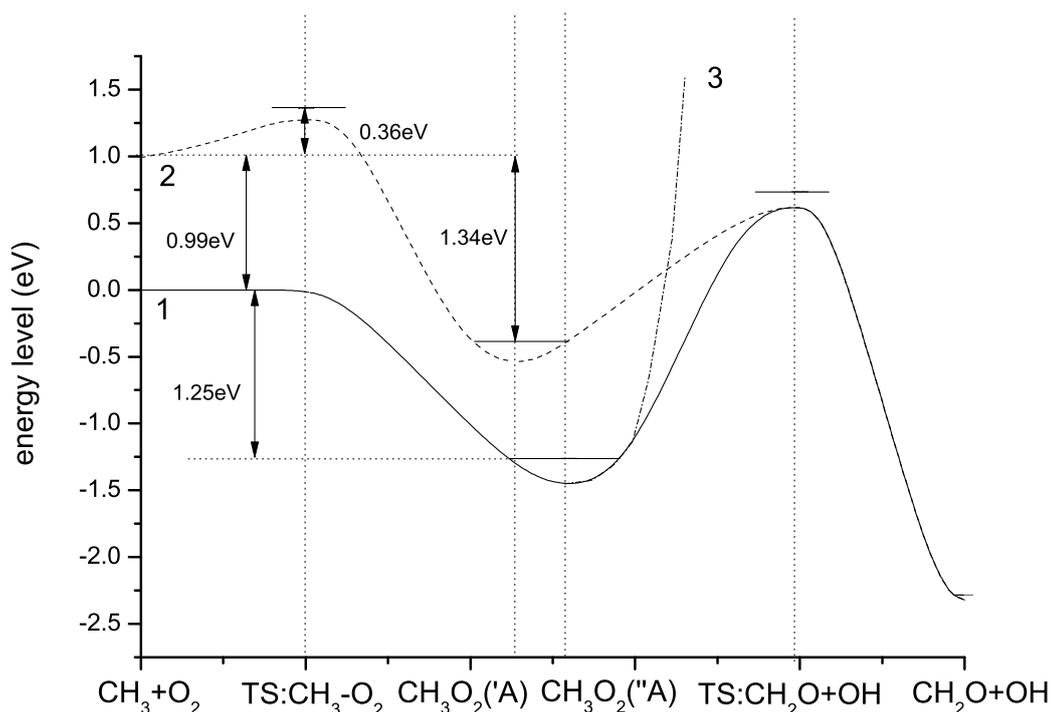


Figure 1: Potential energy surface for the system $\text{CH}_3 + \text{O}_2$. 1 - ground term $^2A''$ corresponding to the reaction with $\text{O}_2(X^3\Sigma_g)$. 2 - excited term $^2A'$ corresponding the reaction with $\text{O}_2(a^1\Delta_g)$. 3 - crossing of terms between CH_3O_2 and the transition state to $\text{CH}_2\text{O} + \text{OH}$

	$A(\frac{cm^3}{s})$	n	$E_a(\frac{kcal}{mole})$
k_{1a}	2.76×10^{-7}	-2.71	8.61
k_{2a}	1.17×10^5	-5.73	4.12
k_{1b}	5.76×10^{-17}	1.63	6.9
k_{2b}	6.85×10^{-20}	2.09	12.11
k_{1c}	1.70×10^{-20}	2.68	6.66
k_{2c}	7.74×10^{-14}	0.71	26.96

Table 2: Rate parameters of reactions from different sources, P=1 atm.

The Potential Energy Surface of the system $CH_3 + O_2(X^3\Sigma;^1\Delta_g)$ was investigated at the multi-reference configuration interaction (MRCI) level of theory [7] in the triple-zeta basis set of Dunning and Hay. The calculated energy of O_2 excitation (0.99 eV) and the well depth of CH_3O_2 in the ground state ($28.6 \frac{kcal}{mole}$ taking ZPE into account) are in good agreement with the experimental values of 0.98 eV in [8] and $28.5 \frac{kcal}{mole}$ in [9] respectively. Figure 1 presents the resulting PES. The activation energy of the process (1a) is as high as 0.28 eV (0.36 eV taking ZPE energies into account).

The rate parameters k_{1a} , k_{1b} , k_{2a} , k_{2b} , k_{1c} , k_{2c} were computed from the data of quantum chemical calculations using the Khimera code [6]. The results are presented in the Table 2, the parameters of rate constant approximation are in the quasi-Arrhenius form.

The reaction for the singlet state is several orders of magnitude slower than the reaction of the triplet state at the characteristic pressure 1 atm. This effect can be explained by the appearance of an energy barrier in the reaction path and by the high probability for CH_3 and $O_2(a^1\Delta_g)$ reaction directly into CH_2O and OH, avoiding stabilization of the way into the methylperoxy radical (CH_3O_2). The reaction rate is three orders of magnitude lower than that from [1], where intuitive suggestions about the PES behavior were used in calculations within the "vibrational term" approach.

The developed model was applied for the simulation of plasma stimulated oxidation of CH_4 . According to common knowledge the most pronounced effect of plasma discharge in air on kinetics is produced by generation of the atomic oxygen [10]. In order to find out the efficiency of the $O_2(a^1\Delta_g)$ we are to compare the influence of both particles on the ignition delay. Since generation of $O_2(a^1\Delta_g)$ in air is not effective [10] the discharge generating this particle was applied to pure oxygen and after the plasma processing the components of the reactive gas were mixed. The effect of the atomic oxygen effect was simulated by the discharge applied to both full mixture and oxygen alone. In all simulations the generation of the desired particle was promoted by adjustment of the reduced electric field strength to the conditions optimal for the desired particles. Generation of atomic oxygen is most effective if the reduced electric field in the discharge is $E/N = 100 - 150$ Td depending on the composition of the gas processed by the plasma while generation of singlet oxygen is most effective when $E/N = 5 - 10$ Td [10]. Since the rate of $O_2(a^1\Delta_g)$ quenching is not reliably known the simulations were performed both with and without the corresponding processes in the kinetic model.

Thus the comparison of following effects was performed:

- Generation of O in pure oxygen ($E/N = 100$ Td).
- Generation of O in air ($E/N = 150$ Td).
- Generation of $O_2(a^1\Delta_g)$ in pure oxygen ($E/N = 10$ Td).

- Generation of $O_2(a^1\Delta_g)$ in pure oxygen ($E/N = 10$ Td) without quenching.
- Input of the energetically equivalent amount of heat.

The results of the comparison with different total plasma energy input are given in Fig. 2. The efficiency of $O_2(a^1\Delta_g)$ is sensitive to the rate of quenching and could potentially be competitive to the reaction with atomic oxygen. The impact of the $O_2(a^1\Delta_g)$ is due to participation to the initiation reaction and reaction k_{1b} . The low rate parameter of the reaction k_{1a} leads to lower ignition delays. Since in the present model CH_3O_2 produced in reaction 1a mainly dissociates into $CH_3 + O_2(X^3\Sigma_g)$ the overall effect of this reaction is the dissipation of the excitation energy into heat $O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma_g)$. In all simulations application of plasma produced greater impact on the ignition delay than heating of the mixture.

The peculiarities of the sub-mechanism of $O_2(a^1\Delta_g)$ consumption developed in this study lead to the effective transfer of energy of electronic excitation to generation of radicals and acceleration of the oxidation. From the results of the kinetic simulations follows the high sensitivity of the model to the rate of quenching of $O_2(a^1\Delta_g)$. Thus, further development of the kinetic model should be performed focusing on the evaluation the rates of $O_2(a^1\Delta_g)$ quenching on the variety of particles present in the mixture.

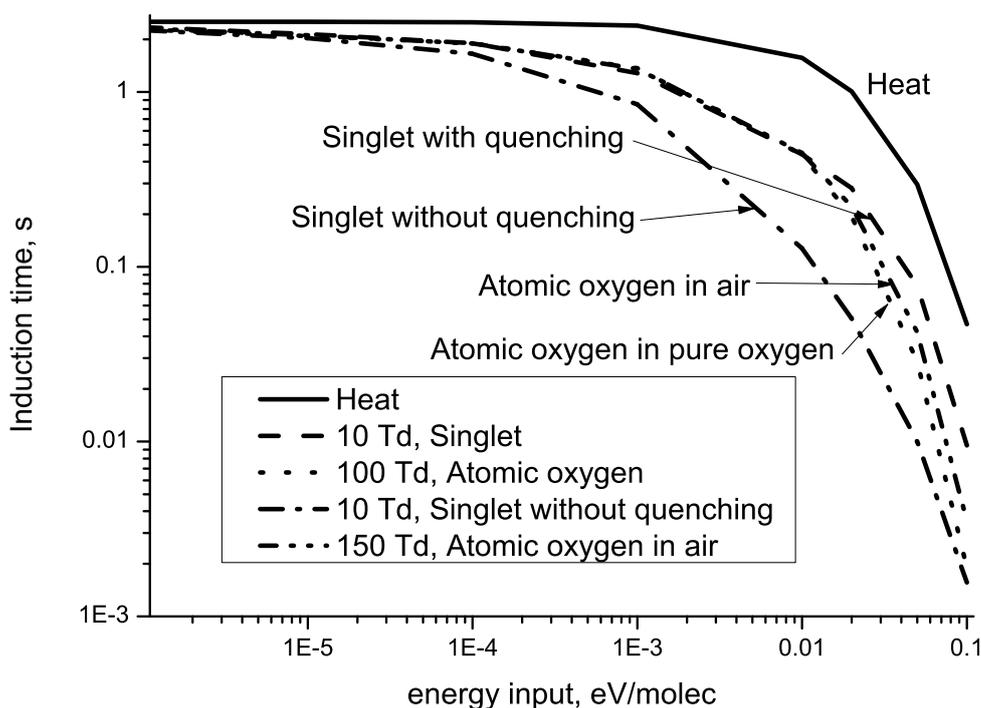


Figure 2: Ignition delay vs plasma energy input at different plasma regimes

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