Interaction of ethane with singlet oxygen: A theoretical study of potential energy surfaces

Alexey V. Pelevkin\(^1,2\) and Alexander S. Sharipov\(^2\)

\(^1\) Moscow Institute of Physics and Technology, Dolgoprudny, Moscow region, Russia
\(^2\) Central Institute of Aviation Motors, Moscow, Russia

E-mail: pelevkin@phystech.edu

Abstract. A study of the \(\text{C}_2\text{H}_6+\text{O}_2\) reaction system was carried out using \textit{ab initio} quantum chemistry methods. The main reaction and quenching channels were identified, corresponding activation energies were calculated, and the pathways of the minimum reaction energy were constructed. It was found that the reaction channels of ethane molecule with singlet delta oxygen proceed with a lower barrier than with the oxygen molecule in the ground state. The reaction of ethane with singlet sigma oxygen, in turn, proceeds through the dissociation of the \(\text{O}_2\) molecule; however, the quenching channel is still possible because of the intersystem crossings. Based on the obtained data, the appropriate reactions rate constants can be estimated by using variational and nonadiabatic transition state theories.

1. Introduction

The practical application of nonequilibrium discharge plasma consisting of highly reactive particles (radicals, ions, vibrationally and electronically excited molecules) for initiation and control of ignition and combustion of various fuels has given rise to special interest among researchers in plasma chemistry and plasma processing during the last decades [1-6]. This is due to the potentially high reactivity of these particles and therefore high efficiency of impact on ignition and combustion processes in comparison with other ways to affect these processes [7, 8]. However, the kinetics of elementary processes with these particles remains insufficiently explored and, in many cases, developing new kinetic mechanisms or complementing the existing ones are required.

One of the key parameters determining processes of formation of reactive particles in an electric discharge plasma is a reduced electric field \(E/N\) \((E – \text{electric field}, N – \text{gas number density})\). Many related works on the discharge plasma processing and plasma-assisted combustion have been carried out dealing with electric gas discharges predominantly at high values of \(E/N\) [1, 2, 5, 9, 10] when the discharge energy goes primarily into the dissociation and the ionization of molecules of fuel or air components. In this case, it is possible to apply conventional thermal equilibrium kinetic schemes for the kinetic simulation of the fuel oxidation. On the other hand, at relatively low \(E/N\) values the electronic states of molecules \(\text{O}_2\) are fairly easily excited [1, 2, 11, 12] (specifically, singlet states of molecular oxygen \(a^1\Delta_g\) and \(b^1\Sigma^+_g\)). In the latter case, the presence of \(\text{O}_2(a^1\Delta_g)\) and \(\text{O}_2(b^1\Sigma^+_g)\) molecules is considered to be critical towards the development of chain initiation and propagation processes for different fuel mixtures [7, 13-15]. It should also be noted that the formation of singlet oxygen may occur under resonant laser radiation [16-18]. In this regard, to evaluate the efficiency of the excitation of electronic states of oxygen \(\text{O}_2\) and interpret experimental data, it is necessary to develop detailed kinetic models that include reactions involving excited \(\text{O}_2\) molecules. However, the existing kinetic data on reaction
rate constants with electronically excited oxygen molecules are very limited or, at best, require critical analysis. This fact complicates the development of appropriate reaction mechanisms and necessitates studying these reactions by theoretical methods.

In this regard, the kinetics of ethane oxidation in a nonequilibrium discharge plasma is of special interest, since ethane is not only interesting in itself as a fuel – its oxidation kinetics underly the reaction mechanisms of ignition and combustion of other hydrocarbons. For these reasons, this paper is dedicated to studying the interaction of an ethane molecule with an oxygen molecule O₂ in the three lowest electronic states – the ground state and the first two singlet states.

2. Methodology

The theoretical study of potential energy surfaces (PESs) of reaction system C₂H₆+O₂(\{X^3Σ^-_g, a^1Δ_b, b^1Σ^-_g^+\}) has been based on a series of quantum chemistry multireference calculations of electronic energy and analysis of the obtained data. The framework method was state-averaged complete active space self-consistent field method (SA-CASSCF) [19] with equal weights for considered states. To refine the energy, pointwise calculations of extended multi-configurational quasi-degenerate second-order perturbation theory (XMCQDPT2) [20] were carried out. For this system active space consists of 12 orbitals with 16 electrons. The Dunning's correlation consistent basis set family with diffuse functions (aug-cc-pVXZ, X=2..4) [21] was used for all multireference calculations throughout this work. All quantum chemistry calculations were implemented using the Firefly QC package [22], which is partially based on the GAMESS (US) [23] source code.

For the considered PESs the spatial structure of reactants, products, and transition states (TS) were optimized at the SA-CASSCF(16,12)/aug-cc-pVDZ level of theory. For optimized structures, a harmonic vibrational frequency analysis at the same level of theory was carried out to verify the number of imaginary frequencies (one imaginary frequency indicates the TS) and to evaluate the zero-point energy (ZPE) contribution to the enthalpy. For each revealed TS, minimum energy pathways (MEP) were constructed by the Gonzalez-Schlegel intrinsic reaction coordinate algorithm [24]. To locate TSs more accurately relative to reactants and products, the IRCMax methodology was applied [25] at the XMCQDPT2(16,12)/aug-cc-pVQZ level of treatment. To reveal possible intersystem crossings (ICs), the vertical projections of the derived MEPs on the adjacent PESs were made. The Lagrange multiplier technique [26] was used to find the structure of the minimum energy crossing point (MECP) that determines quenching processes and spin-forbidden reactions.

3. Results and discussion

The energy diagram of the system C₂H₆+O₂(\{X^3Σ^-_g, a^1Δ_b, b^1Σ^-_g^+\}) obtained by the current multireference methodology is depicted in figure 1. Hereinafter we introduced the designation for transition states (TS) with the left superscript denoting the spin multiplicity and the right subscript labeling the sequence number of given transition states among these of the same multiplicity.

As seen in figure 1, there are two pathways that were discovered earlier in [27]:

\[
\begin{align*}
C₂H₆+O₂(\{X^3Σ^-_g\}) & \rightarrow C₂H₅+HO₂(2^2A'), \quad (R1) \\
C₂H₆+O₂(\{a^1Δ_b\}) & \rightarrow C₂H₅+H₂O₂. \quad (R2)
\end{align*}
\]

A quenching channel was also found for these pathways:

\[
C₂H₆+O₂(\{a^1Δ_b\}) \rightarrow C₂H₅+O₂(\{X^3Σ^-_g\}). \quad (Q1)
\]

Structures of the corresponding TS for processes (R1), (R2), and (Q1) were studied in detail in [27] by using different quantum chemistry methods. Activation energies of these processes were correctly estimated and evaluations of the corresponding rate constants were properly conducted. For this reason, processes (R1), (R2), and (Q1) have not been considered in this paper.

However, two additional pathways with singlet delta oxygen O₂(\{a^1Δ_b\}) that were not found in [27] were observed:

\[
\begin{align*}
C₂H₆+O₂(\{a^1Δ_b\}) & \rightarrow C₂H₅+HO₂(2^2A'), \quad (R3) \\
C₂H₆+O₂(\{a^1Δ_b\}) & \rightarrow C₂H₅+HO₂(2^2A'). \quad (R4)
\end{align*}
\]
Such an oversight in [27] can be explained by the strong multireference nature of singlet oxygen \( \text{O}_2(a' \Delta_g) \) [28]. Some configurations of the \( a' \Delta_g \) state may have been lost in [27] when using single-reference methods (for example, composite method CBS-Q or coupled-cluster method CCSD) and, eventually, pathways (R3) and (R4) were not observed.

On the other hand, because of the twofold orbital degeneracy of \( \text{O}_2(a' \Delta_g) \), the interaction between \( \text{C}_2\text{H}_6 \) and \( \text{O}_2(a' \Delta_g) \) proceeds along two different PESs that leads to the formation of ethyl-radical and \( \text{HO}_2 \) molecule in two different electronic states (\( ^2A'' \) and \( ^2A' \) states corresponding to both PESs). This phenomenon explains the existence of two different pathways (R3) and (R4) for the same reactants (\( \text{C}_2\text{H}_6 \) and \( \text{O}_2(a' \Delta_g) \)).

**Figure 1.** Energy diagram of system \( \text{C}_2\text{H}_6+\text{O}_2 \). Energy values are calculated at the XMCQDPT2/aug-cc-pVQZ // CASSCF(16,12)/aug-cc-pVDZ level of theory with ZPE correction.

On the other hand, because of the twofold orbital degeneracy of \( \text{O}_2(a' \Delta_g) \), the interaction between \( \text{C}_2\text{H}_6 \) and \( \text{O}_2(a' \Delta_g) \) proceeds along two different PESs that leads to the formation of ethyl-radical and \( \text{HO}_2 \) molecule in two different electronic states (\( ^2A'' \) and \( ^2A' \) states corresponding to both PESs). This phenomenon explains the existence of two different pathways (R3) and (R4) for the same reactants (\( \text{C}_2\text{H}_6 \) and \( \text{O}_2(a' \Delta_g) \)).

**Figure 2.** The electronic energy profiles against the intrinsic reaction coordinate for: a) pathway (R3) (black solid curve); b) pathway (R4) (black solid curve) and the profiles obtained during their projection onto the adjacent PESs (dashed curves) at the SA-CASSCF(16,12)/aug-cc-pVDZ level of theory.

To find out possible intersystem crossings along pathways (R3) and (R4), the corresponding MEPs and the projection profiles onto the adjacent PESs were constructed at the SA-CASSCF(16,12)/aug-cc-pVDZ level of theory (see figure 2). As seen in figure 2 there is only one IC along the pathway (R4). This IC point is due to crossing between \( \text{O}_2(a' \Delta_g) \) terms with different orbital quantum numbers. However, since both terms are singlet, their matrix element of spin-orbit coupling is equal to zero. This means that the probability of nonadiabatic transition through this crossing (and the other crossings for these terms) is infinitely small and such ICs can be ignored on estimation the reaction rate constant estimations of the process (R4).
As for the pathway with O$_2$(b$^1\Sigma_g^+$), it was revealed that kinetically favorable reaction pathway proceeds via the dissociation of O$_2$(b$^1\Sigma_g^+$):
\[
\text{C}_2\text{H}_6+\text{O}_2(b^1\Sigma_g^+)\rightarrow\text{C}_2\text{H}_5+\text{O}(^{3}P)+\text{O}^{(3}P).
\] (R5)

However, for this term, the quenching process
\[
\text{C}_2\text{H}_6+\text{O}_2(b^1\Sigma_g^+)\rightarrow\text{C}_2\text{H}_5+\text{HO}_2(^2\Sigma_g^+),
\] (Q2)
caused by nonadiabatic transition between C$_2$H$_6$+O$_2$(b$^1\Sigma_g^+$) and C$_2$H$_6$+O$_2$(a$^1\Delta_g$) terms was found by locating the corresponding MEP.

For reaction channels (R3) and (R4) and for the quenching channel (Q2) the activation energies were calculated within the framework of the described methodology. Values of energy activation (in the forward and backward directions), as well as the values of reaction enthalpy are presented in table 1.

| label | Pathways | $E_a^+$ | $E_a^-$ | $\Delta H^o$ |
|-------|----------|---------|---------|-------------|
| (R1)  | C$_2$H$_6$+O$_2$(X$^3\Sigma_g^-$)→C$_2$H$_5$+HO$_2$(^2\Sigma_g^+) | 2.048$^a$ | 0.255$^a$ | 2.303$^a$ |
| (R2)  | C$_2$H$_6$+O$_2$(a$^1\Delta_g$)→C$_2$H$_5$+H$_2$O$_2$ | 0.497$^a$ | – | – |
| (R3)  | C$_2$H$_6$+O$_2$(a$^1\Delta_g$)→C$_2$H$_5$+HO$_2$(^2\Sigma_g^+) | 1.304 | 0.247 | 1.057 |
| (R4)  | C$_2$H$_6$+O$_2$(a$^1\Delta_g$)→C$_2$H$_5$+HO$_2$(^2\Sigma_g^+) | – | 2.093 | 2.093 |
| (Q1)  | C$_2$H$_6$+O$_2$(a$^1\Delta_g$)→C$_2$H$_6$+O$_2$(X$^3\Sigma_g^-$) | 1.174$^a$ | – | – |
| (Q2)  | C$_2$H$_6$+O$_2$(b$^1\Sigma_g^+$)→C$_2$H$_5$+HO$_2$(^2\Sigma_g^+) | 2.294 | 0.821 | 1.444 |

$^a$ These values were taken from [27].

4. Conclusion
A detailed study of the three lowest electronic states of the C$_2$H$_6$+O$_2$ system was carried out using multi-configuration ab initio quantum chemistry methods. Possible reaction and quenching channels were found, the values of the activation energy of these processes were obtained, pathways of the minimum reaction energy were constructed and possible intersystem crossings and minimum energy crossing points were located.

The revealed processes in the C$_2$H$_6$+O$_2$(X$^3\Sigma_g^-$, a$^1\Delta_g$) system correspond, in general, to the results of previous studies on this system. In particular, reactions with singlet delta oxygen proceed with a significantly lower activation barrier than a reaction with molecular oxygen in the ground state.

Nevertheless, new channels in the C$_2$H$_6$+O$_2$(X$^3\Sigma_g^-$, a$^1\Delta_g$, b$^1\Sigma_g^+$) systems, which can also play an important role in the kinetics of ethane oxidation by singlet oxygen O$_2$(a$^1\Delta_g$) and O$_2$(b$^1\Sigma_g^+$), were detected for the first time. Some of the newly revealed processes lead to the formation of an electronically excited molecule HO$_2$(^2\Sigma_g^+) which kinetics might be of special interest in plasma chemistry researches.

In the future, we are planning to evaluate the rate constants of the newly identified processes in the framework of variational and non-adiabatic transition state theories.

Acknowledgment
This work was supported by the Russian Foundation for Basic Research (project no. 20-38-70014).

References
[1] Starikovskiy A. and Aleksandrov N. 2013 Prog. Energy Combust. Sci. 39 61-110
[2] Starikovskaia S. M. 2014 J. Phys. D: Appl. Phys 47 353001
[3] Adamovich I. V. and Lempert W. R. 2015 Plasma Phys. Control. Fus. 57 014001
[4] Castela M., Fiorina B., Coussement A., Gicquel O., Darabiha N. and Laux C. O. 2016 *Combust. Flame* **166** 133-147
[5] Filimonova E. A., Bocharov A. N., Dobrovolskaya A. S. and Bityurin V. A. 2019 *Plasma Chem. Plasma Process.* **39** 683-694
[6] Weltmann K.-D., Kolb J. F., Holub M., Uhrlandt D., Šimek M., Ostrikov K., Hamaguchi S., Cvelbar U., Černák M., Locke B., Fridman A., Favia P. and Becker K. 2019 *Plasma Process. Polym.* **16** e1800118
[7] Starik A. M., Loukhovitski B. I., Sharipov A. S. and Titova N. S. 2015 *Phil. Trans. R. Soc. A* **373** 20140341
[8] Lu X., Naidis G. V., Laroussi M., Reuter S., Graves D. B. and Ostrikov K. 2016 *Phys. Rep.* **630** 1-84
[9] Lee D. H., Kim K. T., Song Y. H., Kang W. S. and Jo S. 2013 *Plasma Chem. Plasma Process.* **33** 249-269
[10] Ju Y. and Sun W. 2015 *Prog. Energy Combust. Sci.* **48** 21-83
[11] Chen Q., Yang X., Sun J., Zhang X., Mao X., Ju Y. and Koel B. E. 2017 *Plasma Chem. Plasma Process.* **37** 1551-1571
[12] Mao X., Rousseau A., Chen Q. and Ju Y. 2019 *Proc. Combust. Inst.* **37** 5545-5552
[13] Smirnov V. V., Stelmakh O. M., Fabelinsky V. I., Kozlov D. N., Starik A. M. and Titova N. S. 2008 *J. Phys. D: Appl. Phys.* **41** 192001
[14] Vagin N. P., Kochetov I. V., Napartovich A. P. and Yuryshev N. N. 2016 *J. Phys. D: Appl. Phys.* **49** 055505
[15] Vagin N. P., Kochetov I. V., Napartovich A. P. and Yuryshev N. N. 2016 *Bull. Lebedev Phys. Inst.* **43** 211-216
[16] Starik A. M. and Titova N. S. 2003 *Dokl. Phys.* **48** 398-404
[17] Starik A. M., Kozlov V. E. and Titova N. S. 2014 *Energy Fuels* **28** 2170-2178
[18] Starik A. M., Pelevkin A. V. and Titova N. S. 2017 *Combust. Flame* **176** 81-93
[19] Roos B. O. 1987 *Adv. Chem. Phys.* **68** 399-445
[20] Granovsky A. A. 2011 *J. Chem. Phys.* **134** 214113
[21] Kendall R. A., Dunning Jr. T. H. and Harrison R. J. 1992 *J. Chem. Phys.* **96** 6796-6806
[22] Granovsky A. A. Firefly version 8 [http://classic.chem.msu.su/gran/firefly/index.html](http://classic.chem.msu.su/gran/firefly/index.html)
[23] Schmidt M. W., Baldridge K. K., Boatz J. A., Elbert S. T., Gordon M. S., Jensen J. H., Koseki S., Matsunaga N., Nguyen K. A., Su S., Windus T. L., Dupuis M. and Montgomery J. A. 1993 *J. Comput. Chem.* **14** 1347-1363
[24] Gonzalez C. and Schlegel B. H. 1989 *J. Chem. Phys.* **90** 2154-2162
[25] Pelevkin A. V. and Sharipov A. S. 2019 *Plasma Chem. Plasma Process.* **39** 1533-1558
[26] Matsika S. 2007 *Reviews in Computational Chemistry* vol 23, ed Lipkowitz K. B., Cundari T. R. and Boyd D. B. (Hoboken, New Jersey: John Wiley & Sons, Inc.) p 83-124
[27] Sharipov A. S. and Starik A. M. 2012 *J. Phys. Chem. A* **116** 8444-8454
[28] Minaev B. F., Murugan N. A. and Agren H. 2013 *Int. J. Quantum Chem.* **113** 1847-1867