The quest for a detailed comprehension of elementary reactions in combustion: A crossed molecular beam study of the O(^{3}P) reactions with unsaturated C4 hydrocarbons

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The quest for a detailed comprehension of elementary reactions in combustion: a crossed molecular beam study of the O(³P) reactions with unsaturated C4 hydrocarbons

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Abstract. In combustion, the overall chemical changeover is the result of an intricate network of elementary reactions (unimolecular, bimolecular and termolecular) which are classified according to their role (initiation, propagation, branching, termination steps) in the chain reaction. To implement a realistic combustion model, a deep knowledge of the chemical transformation at the molecular level for all the important steps is crucial. In this contribution, the capabilities of the crossed molecular beam (CMB) method with mass spectrometric (MS) detection in the study of multi-channel elementary reactions of relevance in combustion chemistry are illustrated by several examples of reactions involving atomic oxygen and C4 unsaturated hydrocarbons. In particular, the focus will be on the almost unique capability of the CMB-MS method in identifying the reactions products and their branching ratios by means of the same detection scheme and under well-controlled conditions. As expected, the initial steps of the reactions between atomic oxygen and C4 unsaturated hydrocarbons are similar to that of the other reactions that involve O and smaller unsaturated hydrocarbons, as they all feature the attack of the electrophilic O atom to the π density of the multiple bond(s). However, the much more complex molecular structure leads to an increase of the possible reaction channels. Intersystem crossing (ISC) from the triplet potential energy surface to the lower energy singlet one via intersystem crossing is significant and opens, also in this case, several reaction channels which are not otherwise available. Several pairs of products formed after ISC are closed-shell molecules, rather than open-shell radicals. Clearly, this observation has strong implications for combustion modeling, because ISC shifts part of the reactive flux toward terminating rather than propagation or branching steps.

INTRODUCTION

Combustion is a chemical transformation involving a fuel and an oxidizing agent that converts chemical energy into heat. Even in the case of very simple fuels, the overall chemical changeover is actually the result of an intricate network of elementary reactions (unimolecular, bimolecular and termolecular) which are classified according to their role (initiation, propagation, branching, termination steps) in the chain reaction. Therefore, a thorough characterization of combustion processes requires the validation of a robust reaction network for each specific type of fuel, that will be included in combustion models. Combustion models are computer-based mathematical simulations that allow accounting for the physical conditions of the combustion system and the chemical transformation. The latter is represented by the kinetics of all the possible elementary reactions of relevance under the appropriate boundary conditions considered.[1] As a consequence, to implement a realistic combustion model, a deep knowledge of the chemical transformations at the molecular level for all the important steps is crucial.[2] Only in this way is it possible to achieve a complete characterization and, possibly, the control of combustion systems, especially if one is interested in preventing the formation of pollutants which are formed in trace amounts.

Chain propagation and branching steps are bimolecular reactions and involve at least one open-shell reactant. Therefore, bimolecular reactions are at the heart of the chemical transformation in flames. In the last decades, the rate coefficients for most of them have been determined in kinetics experiments, mainly at room temperature or, in some cases, at the temperatures of relevance in combustion.[3] Much less is known, instead, on the chemical identity of the primary products and their branching ratios (BRs). Nevertheless, product yields are important data in the modeling, since the products of one elementary reaction are the reactants of a subsequent one that may be chain propagating or chain terminating and may lead to the formation of different pollutants with very different efficiencies. In the case of relatively complex, multi-channel reactions the primary products are not easy to predict on the basis of chemical intuition and the product BRs must be determined in laboratory experiments.

In the *Laboratory of Molecular Processes in Combustion* at the *University of Perugia*, we make use of the crossed molecular beam (CMB) technique with mass spectrometric (MS) detection to investigate polyatomic multi-channel elementary reactions under single collision conditions.[4,5] This technique, originally developed to address fundamental aspects on reaction mechanisms at the microscopic level,[6,7] has recently been improved to a level that allows one to study polyatomic multi-channel reactions including those of relevance in combustion chemistry at the high temperatures (high collision energy) typical of flames and other combustion environments.[4-10] The CMB-MS technique is based on a collision-free approach, which means that only the collisions of interest are allowed to occur. In CMB experiments on bimolecular reactions, in fact, the two reactants are not simply mixed together, but are confined into distinct supersonic molecular beams with a well-defined velocity and which are made to cross each other at a specific angle. In other words, the atomic/molecular species of each beam collide only with those of the other beam. The products formed by reactive collisions at the collision center are then detected by the mass spectrometer before undergoing secondary or wall collisions (the pressure of the collision chamber is maintained very low so that the mean free path is much larger than the dimensions of the collision chamber and the products fly undisturbed up to the detector).

In conclusion, in this kind of experiments the primary products of many identical, well-defined molecular collisions are recorded and analyzed with the same detection scheme. The absence of further collisions is crucial to establish the real nature of the primary products, because they are normally transient species which, in bulk experiments, could undergo secondary collisions and react further. In general, the CMB-MS technique allows determining *(a)* the nature of the primary reaction products, *(b)* the BRs of competing reaction channels, *(c)* the microscopic reaction mechanisms, and *(d)* the product energy partitioning. The characterization of the reaction mechanism and possible intermediates, as well as of the product energy release, can also help in the modeling of the high temperature/density media of combustion. Reaction intermediates can be collisionally stabilized, while internally hot radicals produced by very exothermic reactions can be much more reactive.

The benefits of the CMB-MS approach support its application to the study of reactions of interest in combustion.[4-11] In our laboratory, we have applied this method to several reactions involving atomic oxygen, O(^{3}P), and small unsaturated hydrocarbons common in flames.[12-21] These reactions play a key role because small unsaturated hydrocarbons are formed during the combustion of most carbon-based fuels. The reactions we have already investigated with the CMB-MS technique are those with C2- and C3-hydrocarbons (ethyne and ethene; propyne, propene and propadiene). The experimental investigation of these systems has often been complemented by the theoretical characterization of the underlying potential energy surfaces (PESs). With the exception of the reaction O(^{3}P) + C$_2$H$_2$, all the other reactive systems have been found to be strongly affected by the occurrence of intersystem crossing (ISC) from the triplet to the lower energy singlet PESs.[13-21] ISC opens new reactive channels which are precluded to the systems if the reactions occur exclusively on the original triplet PES. Since each system has its own characteristics in terms of coupling terms between the triplet and singlet PESs, it is very difficult to extrapolate the results from one system to another, even in the case of very similar hydrocarbons (see, for instance, the case of the two reactions with C$_3$H$_4$ isomers propyne and propadiene[18] or the sequence O(^{3}P)+ethene, propene and 1-butene[22]).

More recently, we have started investigating the reaction of O(^{3}P) with C4-hydrocarbons (namely, 1-butene, 1,2-butadiene and 1,3-butadiene)[19-21,23] and aromatics (namely, benzene and toluene). In this contribution, we present a summary of our results on the reactions O(^{3}P) with the investigated C4 unsaturated hydrocarbons.

EXPERIMENTAL

The main aspects of the CMB approach with MS detection and time-of-flight (TOF) analysis have been already described in many reviews and book chapters. Our apparatus follows the classic design by Lee and Herschbach,[6,7]

with some important improvements.[4,5] In brief, two beams (one of atomic oxygen and one of a specific hydrocarbon) are produced with narrow angular and velocity spreads and crossed at specific collision angles (45°, 90°, 135°) in a high-vacuum collision chamber. A chopper wheel can be placed in front of the detector to measure TOF spectra. Angular and TOF distributions of the products are recorded after the reactive collision takes place. The detector is composed of a tunable electron impact ionizer followed by a quadrupole mass filter. The ionizer is in the innermost part of a triply differentially pumped ultra-high-vacuum chamber. The entire detector unit can be rotated in the collision plane around an axis passing through the collision center. The improvements brought to our CMB instrument have opened new perspectives on reactive scattering studies of polyatomic reactions of relevance in combustion chemistry. In particular, besides the capability of generating intense continuous beams of atomic oxygen and the possibility of increasing the collision energy by changing the collision angle, it is the implementation of the "soft" electron ionization in the MS detector of our CMB instrument that, by permitting to suppress or mitigate the long standing problem, common in this kind of experiments when operating with "hard" (70 eV) electron ionization, of the dissociative ionization of reactants, products and background gases, has led to an increased overall sensitivity which has been crucial for probing all competing product channels of these complex multichannel reactions.[4,5] The main features of our CMB apparatus and recent improvements have been recently detailed elsewhere and will not be further described here.[4,5]

O(^{3}P) REACTIONS WITH C$_4$ UNSATURATED

The reactions investigated in our laboratory involving C4 unsaturated hydrocarbons are similar to those involving C2 and C3 species as far as the initial attack is concerned.[12-23] In all cases, indeed, we have verified that the reactions initiate with the addition of the electrophilic O(^{3}P) to the π system of the unsaturated hydrocarbons. In the case of 1-butene there is only one such attack site, while for 1,2- and 1,3-butadiene there are two double bonds and, therefore, two possible attack sites. However, due to the symmetry of 1,3-butadiene, the two attacks are totally equivalent and the distinction is necessary only for 1,2-butadiene, where the final O-addition can actually occur at three different carbon atoms, to the contrary of 1,3-butadiene and C3 unsaturated hydrocarbons where the O-addition can occur at only two different carbon atoms. Even if they share the attack mechanism, however, C4 hydrocarbons have more complex molecular structures and, therefore, the possible outcomes are more numerous than in the case of C2 and C3 unsaturated hydrocarbons.[19-21,23]

For all three systems, we have identified and characterized numerous reaction channels and their BRs. The experimental results have been accompanied and interpreted in the light of the relevant triplet and singlet PESs. RRKM/ME (Rice-Ramsperger-Kassel-Marcus/Master Equation) statistical calculations of product BRs. The main results can be summarized as follows.

The reaction O(^{3}P) + 1-butene

The reaction O(^{3}P) + 1-butene is of great interest because 1-butene is one of the main products of 1-butanol pyrolysis (accompanied by the loss of one water molecule),[24] a process which largely occurs when burning biobutanol, a very promising biofuel. In addition to that, since we have already investigated the case of ethene and propene, it is interesting to collectively analyse the series of terminal alkenes searching for similarities and differences that can allow generalizations. Because of the increased molecular complexity, there are numerous possible exothermic channels. Previous investigations have derived the global rate coefficients and also (partial) BRs.[25-30] An excursus of the previous results is presented in Table 1, where also the experimental values obtained in our laboratory and the RRKM estimates derived in collaboration with the group of Carlo Cavallotti (Politecnico di Milano, Italy) are reported.

From CMB experiments[19,20] at a collision energy (E_c) of 43.9 kJ/mol, primary products have been detected at mass-to-charge ratios (m/z) of 71 ($C_4H_7O^+$), 70 ($C_4H_6O^+$), 69 ($C_4H_5O^+$), 68 ($C_4H_4O^+$), 43 (CH_3CO^+, $C_3H_7^+$), 42 (CH_2CHO^+), 30 (H_2CO^+), 29 (HCO^+, $C_2H_5^+$), 28 ($C_2H_4^+$, CO^+), 27 ($C_2H_3^+$), and 15 (CH_3^+). For most of these m/z values, LAB angular and TOF distributions were measured. Notably, no reactive signal was detected at m/z = 14 and 17, which rules out (within our sensitivity, i.e., BF ≤ 1-2%) the weakly exoergic channel leading to CH_2 formation and also the H abstraction pathway leading to the OH formation channel. We did not find any indication of the occurrence of the CO + C_3H_8 channel. From the combined experimental/theoretical analysis, we have found that the most important channels are those associated to the formation of two-radicals, namely CH_2CHO(vinoxy) + C_2H_5(ethyl) +, HCO(formyl) + C_3H_7(propyl), and CH_3(methyl) + C_3H_5O (see Table 1). The channel leading to the two close-shell species H_2CO (formaldehyde) + C_3H_6 (propene) is also important (BR of about 0.15), while the channel leading to the

CH$_3$CO(acetyl) + C$_2$H$_5$, the H-displacement channels and the H$_2$-elimination channels have been found to be minor (BR < 0.04). Some of this set of products can only be formed after ISC. Overall, the extent of ISC has been evaluated to be *ca.* 50%, that is quite larger than that estimated for the reaction with propene (25%), but very similar to the one derived for ethene (50%). The analysis of the series of reactions O(^{3}P)+alkenes has permitted us to derive rate rules for the terminal alkene series ranging from propene to dodecene.[22]

TABLE 1. Comparison between the previous, CMB-MS and theoretical results for the product channel branching ratios for the O(^{3}P) + 1-butene reaction.

Product Channel	Blumen-berg et al.[25]	Koda et al.[26]	Quandt et al.[27]	Min et al.[28]	Oguchi et al.[29]	Su et al.[30]	CMB-MS E_c=41.8 kJ/mol	RRKM vs CMB-MS	RRKM 300 K
CH$_2$CHO + C$_2$H$_5$	0.38	1.00	Important	-	0.29 ± 0.05	-	0.34 ± 0.11	0.31	0.32
CH$_3$CO + C$_2$H$_5$							0.014 ± 0.007	0.04	0.06
H-channel	-	-	Very low	-	-	-	0.013 ± 0.004	0.13	0.03
CH$_3$ channel	0.30	-	-	-	0.05 ± 0.01	-	0.28 ± 0.09	0.13	0.18
HCO + C$_3$H$_7$	0.18	0.29 ± 0.07	-	No detection	-	-	0.17 ± 0.06	0.22	0.36
H$_2$CO + C$_3$H$_6$	< 0.135	Mainly secondary product	-	-	-	Important	0.15 ± 0.05	0.13	0.06
H$_2$-channel	0.005-0.038	-	-	-	-	-	0.037 ± 0.015	0.025	0.025

The reaction O(^{3}P) + 1,2-butadiene

We have investigated the reaction O(^{3}P) + 1,2-butadiene at a collision energy of 41.8 kJ/mol and identified nine different product channels. According to the analysis of laboratory distributions there are two dominant molecular channels, one leading to C$_3$H$_6$ + CO (ca. 50%) and one leading to CH$_3$CH(ethylidene) + CH$_2$CO(ketene) (ca. 15%). Several radical forming channels account overall for the remaining 35%. As an example of how TOF data can provide information on distinct product channels for this system, in Fig. 1(a), we report the TOF spectra recorded at the scattering angles of 28° and 44° for *m/z* = 41. At this *m/z* we observed the contribution from seven reactive channels because of the still considerable fragmentation upon electron impact ionization, despite the use of an ionization energy of 17 eV. However, given the different kinematics and reaction dynamics, the seven contributions can be disentangled without ambiguity during the data analysis. For instance, on the basis of energy and linear momentum conservation, the fastest peak is clearly assigned to the channel leading to C$_3$H$_6$ + CO. At large flight times, instead, the fingerprints of the H-displacement and the H$_2$-elimination channels are visible in associations with their heavy co-products C$_4$H$_5$O and C$_4$H$_4$O detected at the mass of their daughter ions. In the TOF spectra are also visible the fingerprints of ketene (CH$_2$CO) and of the vinoxy radical CH$_2$CHO, detected at their daughter ion. Notably, the extent of ISC estimated experimentally is found to be about 70%, which is similar, although somewhat lower, than in the case of the related reaction with propadiene (allene)[15], where it was estimated to be about 90%. A full account of the experimental results accompanied by dedicated electronic structure calculations of the triplet and singlet PESs and RRKM/ME estimates of the BRs taking into account ISC (currently under completion) will be reported in a future comprehensive publication.

The reaction O(^{3}P) + 1,3-butadiene

In the case of the O(^{3}P) + 1,3-butadiene reaction, we have been able to record reactive signal associated to seven channels which are open at the E_c of 35.6 kJ/mol. Notably, 1,3-butadiene is a ubiquitous intermediate in carbon-fuel combustion, known for its toxicity and for being involved in the formation of major soot precursors (e.g. C$_3$H$_3$). Therefore, a sound identification of the primary products and BRs for the O(^{3}P) + 1,3-butadiene reaction is crucial for future improvements of flame modeling. Previous investigations are sparse[31,32] and no information on product BRs is available. From product angular and velocity distribution measurements at different *m/z* ratios, we have identified the main channels being those leading to C$_4$H$_5$O + H, C$_4$H$_4$O + H$_2$, C$_3$H$_6$(propene) + CO, C$_3$H$_5$ + HCO, C$_2$H$_3$ + CH$_2$CHO

(vinoxy), $C_2H_4 + CH_2CO$(ketene), $C_3H_4 + CH_2O$ (formaldehyde), and determined their BRs. As an example of the sensitivity of the experimental data, we show the $m/z = 41$ TOF distribution recorded at the LAB angle of 44° in Fig. 1(b) exploiting soft electron ionization at 17eV. In this case as well, we have been able to disentangle the various contributions during the data analysis. By analyzing the spectrum we can see a fast shoulder, which has been attributed to propene from the $C_3H_6 + CO$ channel, a slower peak attributed to the propenyl radical from the C_3H_5+ HCO channel, and the slowest peak, which has been attributed to both the coproducts of H_2 elimination and H displacement channels. Also for this system the extent of ISC is ≥70%. Dedicated electronic structure calculations of the underlying triplet/singlet PESs and related RRKM/Master Equation estimates of the BRs, with inclusion of ISC, are currently under way by C. Cavallotti, and a full account of this synergistic experimental/theoretical work will be reported in the near future.
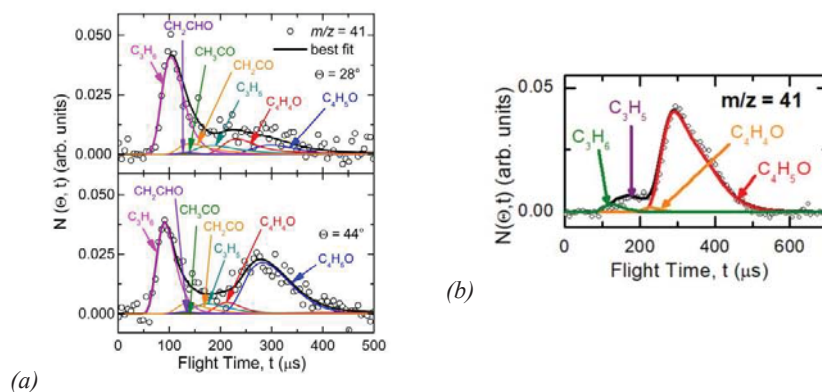

FIGURE 1. Time-of-flight distributions at the indicated m/z= 41 recorded *(a)* for the O+1,2-butadiene reaction at Θ = 28° and 44° and (b) for the O+1,3-butadiene reaction at Θ= 44°. The contributions arising from each reaction channels, as determined during the data analysis, are also shown (see labels).[33,34]

CONCLUSION

In this contribution, an extension of the CMB-MS technique to the case of the reactions between O(^{3}P) and C4 unsaturated hydrocarbons is presented. As expected, the initial steps of these reactions are similar to those of the other reactions that involve atomic oxygen and smaller unsaturated hydrocarbons, as they all feature the attack of the electrophilic O atom to the π density of the multiple bond(s). However, the much more complex molecular structure of C4 unsaturated hydrocarbons leads to an increase of the possible reaction channels. ISC is seen to occur and to open, also in this case, several reaction channels which are not available on the triplet PES. To be noted that several pairs of products formed after ISC are two closed-shell molecules, rather than open-shell radicals. Clearly, this observation has strong implications for combustion modeling, because ISC shifts part of the reactive flux toward terminating steps rather that propagation or branching steps.

ACKNOWLEDGMENTS

REFERENCES

1.   W.C. Gardiner Jr, *Gas-phase combustion chemistry* (Springer-Verlag, New York, 2000).
2.   S. A. Carl, L. Vereecken, J. Peeters, Phys. Chem. Chem. Phys. **9**, 4071-4084 (2007).

3. D. L. Baulch, C. T. Bowman, C. J. Cobos, R. A. Cox, Th. Just, J. A. Kerr *et al*., J. Phys. Chem. Ref. Data **34**, 757-1397 (2005).
4. P. Casavecchia, F. Leonori, N. Balucani, R. Petrucci, G. Capozza, E. Segoloni, Phys. Chem. Chem. Phys. **11**, 46–55 (2009).
5. P. Casavecchia, F. Leonori, N. Balucani, Int. Rev. Phys. Chem. **34**, 161–204 (2015).
6. Y. T. Lee, "Reactive scattering I: non-optical methods", in *Atomic and molecular beam methods,* edited by G. Scoles (Oxford University Press, New York, 1987), pp. 553-568.
7. M. Brouard and C. Vallance, *Tutorials in molecular reaction dynamics* (Royal Society of Chemistry Publishing, Cambridge, 2010).
8. A.M. Mebel and R.I. Kaiser, Int. Rev. Phys. Chem. **17**, 21564-21575 (2015).
9. D. R. Albert, M. A. Todt, H. F. Davis, J. Phys. Chem. A **117**, 13967–13975 (2013).
10. R. I. Kaiser and N. Balucani, Acc. Chem. Res. **50**, 1154−1162 (2017).
11. H. Pan, K. Liu, A. Caracciolo, P. Casavecchia, Chem. Soc. Rev. **46**, 7517 – 7547 (2017).
12. F. Leonori, N. Balucani, G. Capozza, E. Segoloni, G.G. Volpi, P. Casavecchia, Phys. Chem. Chem. Phys. **16**, 10008–10022 (2014).
13. B. Fu, Y.C. Han, J.M. Bowman, L. Angelucci, N. Balucani, F. Leonori, P. Casavecchia, Proc. Natl. Acad. Sci. USA **109**, 9733–9738 (2012).
14. N. Balucani, F. Leonori, P. Casavecchia, B. Fu, J.M. Bowman, J. Phys. Chem. A **119**, 12498–12511 (2015).
15. F. Leonori, A. Occhiogrosso, N. Balucani, A. Bucci, R. Petrucci, P. Casavecchia, J. Phys. Chem. Lett. **3**, 75–80 (2012).
16. G. Vanuzzo, N. Balucani, F. Leonori, D. Stranges, V. Nevrly, S. Falcinelli, A. Bergeat, P. Casavecchia, C. Cavallotti, J. Phys. Chem. A **120,** 4603–4618 (2016).
17. F. Leonori, N. Balucani, V. Nevrly, A. Bergeat, S. Falcinelli, G. Vanuzzo, P. Casavecchia, C. Cavallotti, J. Phys. Chem. C **119,** 14632–14652 (2015).
18. G. Vanuzzo, N. Balucani, F. Leonori, D. Stranges, S. Falcinelli, A. Bergeat, P. Casavecchia, I. Gimondi, C. Cavallotti, J. Phys. Chem. Lett. **7**, 1010–1015 (2016).
19. A. Caracciolo, G. Vanuzzo, N. Balucani, D. Stranges, C. Cavallotti, P. Casavecchia, Chem. Phys. Letters **683**, 105–111 (2017).
20. A. Caracciolo, G. Vanuzzo, N. Balucani, D. Stranges, P. Casavecchia, L. Pratali Maffei, C. Cavallotti, J. Phys. Chem. A **123**, 9934-9956 (2019).
21. A. Caracciolo, G. Vanuzzo, N. Balucani, D. Stranges, S. Tanteri, C. Cavallotti, P. Casavecchia, Chinese J. Chem. Phys. **32**, 113 (2019).
22. L. Pratali Maffei, C. Cavallotti, A. Caracciolo, N. Balucani, P. Casavecchia, Fuel **263**, 116536 (2020).
23. A. Caracciolo, G. Vanuzzo, P. Recio, N. Balucani, P. Casavecchia, Rendiconti Lincei. Scienze Fisiche e Naturali **30**, 549–561 (2019).
24. M. Rosi, D. Skouteris, N. Balucani, C. Nappi, N. Faginas Lago, L. Pacifici, S. Flacinelli, D. Stranges, Frontiers in Chemistry **7**, 326 (2019).
25. B. Blumenberg, K. Hoyerman, R. Sievert, in: Sixteenth Symposium (International) on Combustion, The Combustion Institute, 1976, pp. 841–852.
26. S. Koda, Y. Endo, S. Tsuchiya, E. Hirota, J. Phys. Chem. **95**, 1241–1244 (1991).
27. R. Quandt, Z. Min, X. Wang, R. Bersohn, J. Phys. Chem. A **102**, 60–64 (1998).
28. T. Oguchi, A. Ishizaki, Y. Kakuta, H. Matsui, A. Miyoshi, J. Phys. Chem. A **108**, 1409–1416 (2004).
29. Z. Min, T.-H. Wong, R. Quandt, R. Bersohn, J. Phys. Chem. A **103**, 10451-10453 (1999).
30. H.M. Su, S. Zhao, K. Liu, T. Xiang, J. Phys. Chem. A **111**, 9600–9605 (2007).
31. R. Atkinson and J. N. Pitts, J. Chem. Phys. **67**, 2492–2495 (1977).
32. C. W. Zhou, Y. Li, U. Burke, C. Banyon, K. P. Somers, S. Ding, S. Khan, J. W. Hargis, T. Sikes, O. Methieu, E. L. Petersen, M. Al Abbad, A. Farooq, Y. Pan, Y. Zhang, Z. Huang, J. Lopez, Z. Loparo, S. S. Vasu, H. J. Curran, Combust Flame **197**, 423–438 (2018).
33. A. Caracciolo, PhD Thesis, University of Perugia (2019).
34. P. Recio, PhD Thesis, University of Perugia (2020).