

# The reaction of atomic oxygen with terminal alkenes: the effect of intersystem crossing and the relevance of the formaldehyde production channel

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Because of their relevance in combustion, the rate coefficients for the reactions between ground state  $^3\text{P}$  oxygen atoms and alkenes have been determined in kinetics experiments as a function of temperature. Much less is known, instead, on the chemical identity of the primary products and their branching ratios (BRs). This piece of information is fundamental, because the products of one elementary reaction are the reactants of a subsequent one in the complex scheme of elementary reactions that account for the global combustion process [1]. For multichannel reactions like  $\text{O}(^3\text{P})+\text{alkenes}$ , the primary products and their BR are not easy to guess because intersystem crossing (ISC) from the triplet to the underlying singlet potential energy surface (PES) can occur, opening up other reaction channels not accessible on the triplet PES. The quantification of ISC as a function of temperature is a demanding task. For this reason, we have undertaken a systematic experimental investigation of this class of reactions by means of the crossed molecular beam technique [2] with mass spectrometric detection (CMB-MS). We remind that the CMB-MS technique permits one to (i) investigate bimolecular reactions under truly single-collision conditions, avoiding the complications of a multiple-collision environment and wall effects; (ii) verify unambiguously to which channel belongs a given product detected at a given  $m/z$  ratio; and (iii) assess the presence of potential energy barriers [1,2].

The capabilities of this experimental technique have been well illustrated in the recent study of the  $\text{O}+\text{C}_2\text{H}_4$  reaction where ISC was found to be very efficient and to account for about 50% of the reaction products. The experimental results have been validated by an accurate quasiclassical trajectory study on a reliable global ab initio PES [3,4]. The product BR and the extent of ISC have been quantified as a function of the available energy. The production of formaldehyde (formed adiabatically in the triplet PES in conjunction with  $\text{CH}_2$ ) accounts for ca. 20% at  $E_c=35.1$  kJ/mol [3,4].

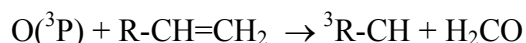
The reactions with higher alkenes (namely, propene and 1-butene) are much more complex because of the presence of additional alkyl groups. For instance in the reaction  $\text{O}+\text{C}_3\text{H}_6$  there are nine possible reaction channels [5,6], while for the reaction  $\text{O}+\text{C}_3\text{H}_8$  there are eleven possible reaction channels (without counting isomeric products) [7].

By combining CMB-MS experiments at  $E_c=38.9$  kJ/mol with high-level ab initio electronic structure calculations of the underlying triplet/singlet PESs and statistical (RRKM/Master Equation) computations of BRs including ISC as a function of temperature and pressure [5,6], we have found that the reactive interaction of  $\text{O}(^3\text{P})$  with

propene mainly breaks apart the 3-carbon atom chain, producing the radical products  $\text{CH}_3 + \text{CH}_2\text{CHO}$  (32%),  $\text{C}_2\text{H}_5 + \text{HCO}$  (9%), and molecular products  $\text{C}_2\text{H}_4 + {}^3\text{CHCH}_3 + \text{H}_2\text{CO}$  (44%). Two isomers,  $\text{CH}_3\text{CHCHO}$  (7%) and  $\text{CH}_3\text{COCH}_2$  (5%), were also observed from H atom elimination, reflecting O-atom attack to both terminal and central C-atoms of propene. Some methylketene (3%) was also formed with  $\text{H}_2$  elimination. As some of these products can only be formed via ISC from the triplet to the singlet PESs, from BRs an extent of ISC of about 22% was inferred. This value is significantly lower than recently observed in  $\text{O}({}^3\text{P}) + \text{C}_2\text{H}_4$  (~50%) at similar  $E_c$ , posing the question of how important it is to consider nonadiabatic effects for these and similar combustion reactions and, in particular, warning that extrapolation of the extent of ISC along a series is not warranted [2]. Comparison of the CMB BRs with those from the recent kinetics studies at 300 K with synchrotron radiation detection [8] and from the RRKM/ME statistical predictions has provided information on the variation of BRs with  $E_c$ . ISC is estimated to decrease from about 60% at 300 K to about 20% when  $E_c$  increases to about 40 kJ/mol [6].

From our preliminary data on the reaction  $\text{O}({}^3\text{P}) + 1\text{-butene}$ , we have got evidence that six reactive channels are open, namely those producing  $\text{C}_2\text{H}_5\text{CHCHO} + \text{H}$ ,  $\text{C}_2\text{H}_5\text{CHCO} + \text{H}_2$ ,  $\text{C}_3\text{H}_5\text{O} + \text{CH}_3$ ,  $\text{CH}_2\text{CHO} + \text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7 + \text{HCO}$ ,  ${}^3\text{CH}_3\text{CH}_2\text{CH} / {}^1\text{CH}_3\text{CHCH}_2 + \text{H}_2\text{CO}$ . Also for this system, the preliminary analysis of the scattering data suggests a significant role of the  $\text{H}_2\text{CO}$  formation channel.

The observation that at combustion temperatures the reactions of  $\text{O}({}^3\text{P})$  with terminal alkenes directly leads to significant formation of formaldehyde, an important pollutant, is an unexpected result that can have significant practical implications. Based on these studies, we proposed a generalized scheme for a new channel of this family of reactions:



which should be significant under the high energy/temperature conditions of combustion systems.

## References

- [1] N. Balucani, F. Leonori, and P. Casavecchia, *Energy*. 43, 47 (2012).
- [2] P. Casavecchia, F. Leonori, and N. Balucani, *Int. Rev. Phys. Chem.* 34, 161 (2015).
- [3] B. Fu, Y.-C. Han, J.M. Bowman, L. Angelucci, N. Balucani, F. Leonori, and P. Casavecchia, *Proc. Nat. Acad. Sci. U.S.A.* 109, 9733 (2012).
- [4] B. Fu, Y.-C. Han, J.M. Bowman, F. Leonori, N. Balucani, L. Angelucci, A. Occhiogrosso, R. Petrucci and P. Casavecchia, *J. Chem. Phys.* 137, 22A532 (2012).
- [5] C. Cavallotti, F. Leonori, N. Balucani, V. Nevrlly, A. Bergeat, S. Falcinelli, G. Vanuzzo, and P. Casavecchia, *J. Phys. Chem. Lett.* 5, 4213 (2014).
- [6] F. Leonori, N. Balucani, V. Nevrlly, A. Bergeat, S. Falcinelli, G. Vanuzzo, P. Casavecchia, and C. Cavallotti, *J. Phys. Chem. C* in press. doi: 10.1021/jp512670y.
- [7] H. Zhao, L. Pan, W. Bian, *Int. J. Quantum Chem.* 112, 858 (2012).
- [8] J.D. Savee, O. Welz, C.A. Taatjes, and D.L. Osborn, *Phys. Chem. Chem. Phys.* 14, 10140 (2012).
- [9] G. Vanuzzo, N. Balucani, S. Falcinelli, D. Stranges, P. Casavecchia, in preparation.