Reactions of oxygen atoms with aliphatic and aromatic hydrocarbons by crossed beam experiments

Nadia Balucani

DCBB, Università degli Studi di Perugia, Perugia - Italy

E-mail: nadia.balucani@unipg.it

Because of their relevance in combustion and other gaseous media, the rate coefficients for the reactions between ground state 3P oxygen atoms and unsaturated hydrocarbons 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, however, 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 these, the primary products and their BR are not easy to predict 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 which requires an experimental or theoretical investigation.

For this reason, following the pioneering work of Y.T. Lee and coworkers [2], we have undertaken a systematic experimental investigation of this class of reactions by means of the crossed molecular beam technique [3] with mass spectrometric detection empowered by soft electron impact ionization. Results on the reactions of atomic oxygen with alkynes [4], alkenes [5], dienes [6], and arenes (benzene and toluene) will be presented. Implications in combustion chemistry will be noted.

References

[1] N. Balucani, F. Leonori, P. Casavecchia, Energy, 43, 47 (2012).

[2] A.M. Schmoltner, P.M. Chu, Y.T. Lee, J. Chem. Phys., 91, 5365 (1989); A.M. Schmoltner, P.M. Chu, R.J. Brudzynski, Y.T. Lee, J. Chem. Phys., 91, 6926 (1989); A.M. Schmoltner, S.Y. Huang, R.J. Brudzynski, P.M. Chu, Y.T. Lee, J. Chem. Phys., 99, 1644 (1993).

[3] P. Casavecchia, F. Leonori, and N. Balucani, Int. Rev. Phys. Chem. 34, 161 (2015).

[4] F. Leonori et al., Phys. Chem. Chem. Phys., 16, 10008 (2014); N. Balucani et al., Chem. Phys. Lett., 602, 58 (2014); G. Vanuzzo et al., J. Phys. Chem. A, 120, 4603 (2016); G. Vanuzzo et al., J. Phys. Chem. Lett., 7, 1010 (2016).

[6] B. Fu et al., PNAS, 109, 9733 (2012); N. Balucani et al., J. Phys. Chem. A, 119, 12498 (2015); C. Cavallotti et al., J. Phys. Chem. Lett., 5, 4213 (2014); Cavallotti et al., J. Phys. Chem. C, 119, 14632 (2015); A. Caracciolo et al., Chem. Phys. Lett., 683, 105 (2017).

[8] F. Leonori et al., J. Phys. Chem. Lett., 3, 75 (2012); A. Caracciolo et al., in preparation.