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Master Equation modelling: Formaldehyde Photophysical Oxidation

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Abstract

For H_2CO photolysis, IUPAC reports quantum yields for radical formation by photons with 10 kJ/mol less energy than that required to form radicals (i.e. < 363 kJ/mol) [IUPAC 2013]. A hypothesis that the reaction between formaldehyde and O_2 could occur after absorption of light, with energy below that required for production of radicals, by a light-driven mechanism is proposed and the following process (R1) is analysed:
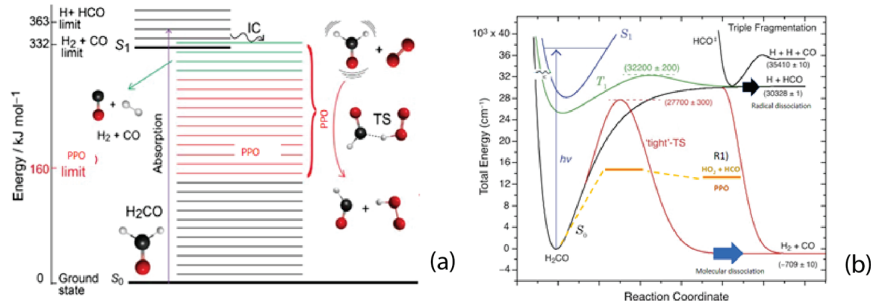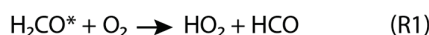
$$H_2CO^* + O_2 \longrightarrow HO_2 + HCO \qquad (R1)$$

Fig. 1. (a) H_2CO^* production after absorption of a near-UV photon [Jordan, Kable, Fisher ARC(DP22)]. (b) ME simulated processes [modified from Quinn 2017]

Molecular oxygen would react with parent carbonyl molecules providing a new HO_2 source. This process is named Photophysical Oxidation (PPO). PPO reaction of the simplest carbonyl, H_2CO, is examined computationally and experimentally.

A Master Equation (ME) model was developed taking into account four processes illustrated in Fig. 1b (i) Internal Conversion (IC) from $H_2CO(S_1)$ to $H_2CO(S_0)$, (ii) molecular and (iii) radical dissociation and (iv) formaldehyde PPO. Rate coefficients for the various reactions were predicted using RRKM theory or Barker and co-workers' semimicrocanonical transition state theory [Maranzana 2007]. These were used within master equation models to assess the importance of (R1) and to simulate recent experimental results. The atmospheric implications of (R1) are also discussed.

References

IUPAC (2013) Task Group on Atmospheric Chemical Kinetic Data Evaluation (Data Sheet P1) (http://iupac.pole-ether.fr)

ARC(DP22) – S. Kable, M. Jordan, J. Fisher

Quinn, M. S., D. U. Andrews, K. Nauta, M. J. T. Jordan and S. H. Kable (2017). The energy dependence of CO(v,J) produced from H_2CO via the transition state, roaming, and triple fragmentation channels. *J. Chem. Phys*. 147, 013935. doi:10.1063/1.4983138

Maranzana, A., J. R. Barker and G. Tonachini (2007). Master equation simulations of competing unimolecular and bimolecular reactions: application to OH production in the reaction of acetyl radical with O2. *Phys. Chem. Chem. Phys*. 9, 4129–4141. doi:10.1039/B705116F