

## A kinetic study of the gas phase reaction between HO<sub>2</sub> radicals and HCHO

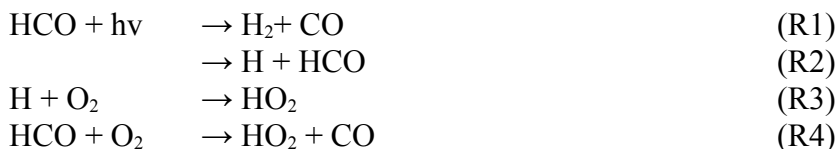
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Formaldehyde (HCHO) is an important indicator of tropospheric hydrocarbon emissions and photochemical activity. It is a principal intermediate in the oxidation of hydrocarbons in the troposphere. Hence it is considered as an important compound for determining the oxidative capacity of the atmosphere. The mechanism by which formaldehyde is photo-oxidized in the troposphere has been the subject of many investigations. It is well understood that the photolysis of formaldehyde occurs according to one of the following two pathways (R1) and (R2) and the subsequent reaction of H and HCO with O<sub>2</sub> produces HO<sub>2</sub> radicals.



The reaction of HO<sub>2</sub> radicals with carbonyl compounds has been proposed as a major sink for carbonyl compounds in the Upper Troposphere / Lower Stratosphere (UTLS). These reactions proceed through a hydrogen bound intermediate before isomerizing into a hydroxyalylperoxy radical. Formaldehyde serves as a prototype for this class of reaction:



Previous measurements of this equilibrium have used either FTIR spectroscopy of end products [1] or via absorption of the B-X band of the direct reaction product, hydroxymethylperoxy (HMP) [2, 3]. However, these measurements are fairly indirect and might have been affected by possible interferences from other species (HO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub>) within the structure less B-X transition of HMP. Recent results [4] have directly detected HMP on the A-X electronic transition and on the ν<sub>1</sub> vibrational OH stretch transition using CRDS. They have found considerable disagreements with the above mentioned literature values.

In this work we will present direct measurements of the equilibrium (R5) through a selective and sensitive detection of HO<sub>2</sub> radicals by cw-CRDS coupled to laser photolysis. The CH<sub>2</sub>O concentration was determined from the known rate constant of its reaction with OH, i.e. through measurement of the pseudo-first order decay of OH radicals by LIF. CH<sub>2</sub>O concentrations could also be determined by direct measurement of their absorption in the near IR by cw-CRDS.

### References

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