

Gas Phase Reaction of CH₃O₂ Radicals with OH Studied over the 292 – 526 K Temperature Range

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Methyl peroxy radical, CH₃O₂, plays important role as a reaction intermediate in the low-temperature combustion and atmospheric oxidation of hydrocarbons. One of the potential pathways for the consumption of methyl peroxy radicals (CH₃O₂) in atmospheric chemistry is the reaction with hydroxyl radical, OH.¹



There is only very limited information on the kinetics and branching ratios in reaction 1. In the only recent direct study of reaction 1, Bossolasco et al.² employed laser induced fluorescence coupled with the cw-cavity ring down spectroscopy. The reported rate constant is large, $k_1 = (2.8 \pm 1.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (294 K, 50 Torr and 100 Torr of helium bath gas) (Figure 1, solid circle).

In this work, methyl peroxy radicals were produced by photolysis of acetone at 193.3 nm (ArF excimer laser) in the presence of molecular oxygen. Hydroxyl radicals were produced in a very fast reaction of O(¹D) atoms, produced in the photolysis of N₂O, with H₂O. The photolysis system is gaseous mixture of acetone/H₂O/N₂O/O₂/He. Kinetics of hydroxy radicals were monitored via transient absorption of light from a DC H₂O/Ar low-pressure resonance lamp at ca. 308 nm.

The overall rate constant of reaction 1 over the 292 – 526 K temperature range and 1 bar helium pressure is:

$$k_1 = (8.3 \pm 1.7) \times 10^{-11} (T / 298 \text{ K})^{-0.77} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (292 - 526 \text{ K}).$$

The branching ratio of channel 1b at 298 K is less than 5%. The rate constant measured in this work is ca. 3.4 times lower than that reported in Ref.²

1. Archibald, A. T.; Petit, A. S.; Percival, C. J.; Harvey, J. N.; Shallcross, D. E. *Atmos. Sci. Lett.* **2009**, 10 (2), 102-108.
2. Bossolasco, A.; Faragó E. P.; Schoemaeker, C.; Fittschen, C. *Chem. Phys. Lett.* **2014**, 593, 7-13.

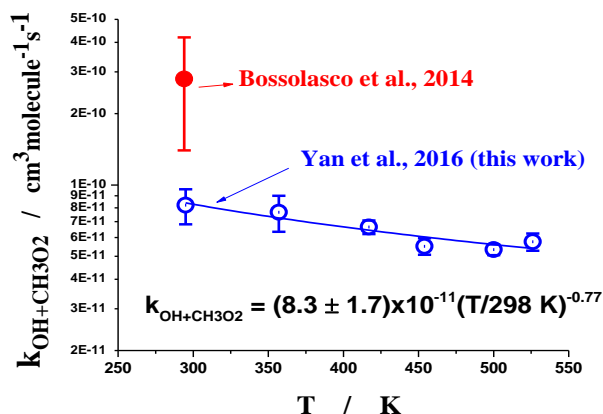


Figure 1