

# A new method for CH<sub>3</sub>O<sub>2</sub> radical detection and kinetic studies of the CH<sub>3</sub>O<sub>2</sub> self-reaction in HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry)

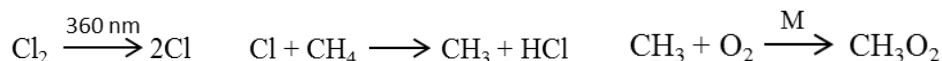
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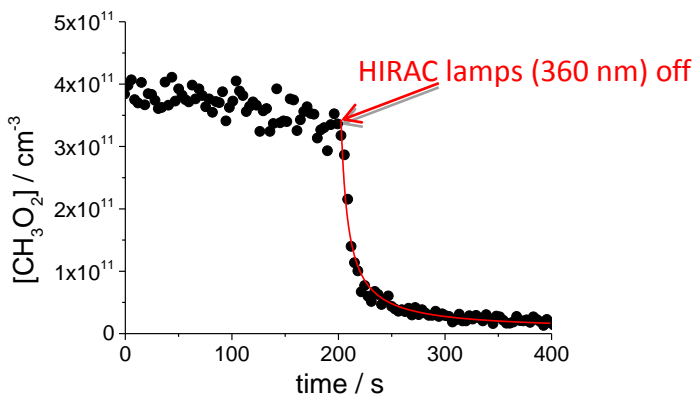
A new method has been developed for the detection of CH<sub>3</sub>O<sub>2</sub> radicals by FAGE (Fluorescence Assay by Gas Expansion) by titrating CH<sub>3</sub>O<sub>2</sub> to CH<sub>3</sub>O by reaction with added NO and then detecting the resultant CH<sub>3</sub>O by laser induced fluorescence. The limit of detection of the technique is [CH<sub>3</sub>O<sub>2</sub>] ~7 × 10<sup>8</sup> molecule cm<sup>-3</sup> for a signal-to-noise ratio of 2 and 1 min averaging time. The method has been used for time-resolved monitoring of CH<sub>3</sub>O<sub>2</sub> during its self-reaction within HIRAC at 1 bar and room temperature to determine a rate coefficient of (2.3 ± 0.57) × 10<sup>-13</sup> s<sup>-1</sup> molecule<sup>-1</sup> cm<sup>3</sup> (Figure 1), which has error bars overlapping with the range of the previous results, (2.7 – 5.2) × 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>1</sup> CH<sub>3</sub>O<sub>2</sub> radicals have been generated in HIRAC by the succession of the reactions:



In addition to detection of CH<sub>3</sub>O<sub>2</sub>, products of the CH<sub>3</sub>O<sub>2</sub> self-reaction were also observed for the two reaction channels (a) and (b) over a range of temperatures from 296 – 340 K:

(a) 2CH<sub>3</sub>O<sub>2</sub> → CH<sub>2</sub>O + CH<sub>3</sub>OH; (b) 2CH<sub>3</sub>O<sub>2</sub> → 2CH<sub>3</sub>O + O<sub>2</sub>,

namely CH<sub>3</sub>O and HO<sub>2</sub> radicals (from reaction of CH<sub>3</sub>O + O<sub>2</sub>) monitored by FAGE, formaldehyde measured by FAGE, and FTIR and methanol observed by FTIR. A good agreement has been obtained between the FTIR and FAGE measurements of CH<sub>2</sub>O. Using the concentrations of CH<sub>3</sub>OH and CH<sub>2</sub>O, the branching ratio for channel (a) at room temperature has been determined as  $r_a = 0.66 \pm 0.06$ . The result is in very good agreement with the value recommended in the review of Tyndall *et al.*<sup>2</sup> of  $r_a = 0.63 \pm 0.06$ . Little temperature dependence of  $r_a$  has been observed from 296 K to 340 K.



**Figure 1.** Second order decay of methylperoxy (CH<sub>3</sub>O<sub>2</sub>) radical concentration monitored by FAGE during the CH<sub>3</sub>O<sub>2</sub> self-reaction in HIRAC.

## References

- (1) <http://iupac.pole-ether.fr/>
- (2) G. S. Tyndall *et al.*, J. Geophys. Res. **2016**, 106, 12157.