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A new method for speciated CH_3O_2 radical detection and HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry) studies of the CH_3O_2 self-reaction

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A new method has been developed for the speciated detection of CH_3O_2 radicals by FAGE (Fluorescence Assay by Gas Expansion) by titrating CH_3O_2 to CH_3O by reaction with added NO and then detecting the resultant CH_3O by LIF (laser induced fluorescence). The limit of detection of the technique is $\sim10^8$ cm^{-3} CH_3O_2 for a unity signal-to-noise ratio and 5 min averaging time. The method has been used for time monitoring of CH_3O_2 during its self-reaction within HIRAC at 1 bar and room temperature to determine a preliminary value of the rate coefficient of 4.2×10^{-13} cm^3 s^{-1}, which lies in the range of the previous results, $(2.7 – 5.2) \times 10^{-13}$ cm^3 s^{-1}.[1]

In addition to detection of CH_3O_2, products of the CH_3O_2 self-reaction were also observed for the two reaction channels over a range of temperatures from 260 – 320 K:

(a) $2CH_3O_2 \rightarrow CH_2O + CH_3OH$; (b) $2CH_3O_2 \rightarrow 2CH_3O + O_2$,

namely HO_2 radicals (from reaction of $CH_3O + O_2$) and formaldehyde monitored by FAGE and formaldehyde and methanol observed by FTIR. A good agreement has been obtained between the FTIR and FAGE measurements of CH_2O which increased to $\sim$ 2 ppmv over the experiments. Using the concentrations of CH_3OH and CH_2O, 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.*[2] of $r_a = 0.63 \pm 0.06$. No temperature dependence of r_a has been observed from 296 K to 321 K.

1. http://iupac.pole-ether.fr/

2. G. S. Tyndall *et al.*, J. Geophys. Res. **106**, 12157 (2001).