Pressure and Temperature Dependent Study of the CH₃C(O)O₂ + HO₂ Reaction Branching Ratio Using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC)

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Organic peroxy radicals, RO₂, play a key role in the tropospheric HO_x (OH and HO₂) cycle. Oxidation of Volatile Organic Compounds (VOCs) lead to the creation of RO₂ and HO₂ radicals. These products are known to react together, with three possible pathways: (A), (B) and (C). The branching ratio for these reactions is dependent on the structure of the RO₂ radicals.

$$\begin{array}{rcl} \mathrm{HO}_2 \ + \ \mathrm{RO}_2 & \rightarrow & \mathrm{ROOH} \ + \ \mathrm{O}_2 & & (\mathbf{A}) \\ & \rightarrow & \mathrm{ROH} \ + \ \mathrm{O}_3 & & (\mathbf{B}) \end{array}$$

 \rightarrow OH + RO + O₂ (C)

Carbonyl containing RO_2 radicals have previously been believed to pass exclusively through reactions (A) and (B), both radical termination channels.^[1] However, recent research has shown that significant OH regeneration, (C), is also possible.^[2] The acetyl peroxy radical (CH₃C(O)O₂) is of particular importance as it is an isoprene (C₅H₈) oxidation product, the major constituent of biogenic emissions from large forested areas and studies of the title reaction should help to our understanding of isoprene oxidation in low NO_x environments.

The reaction of $CH_3C(O)O_2$ with HO_2 has been studied at 292 and 325 K and at 200 and 760 Torr using $Cl_2/CH_3OH/CH_3CHO$ mixtures in the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC) at the University of Leeds. Reactants and products of channels (A) and (B) were measured using FTIR spectrometry (Bruker IFS 66) and a commercial O_3 analyser (Thermo 49C) while channel (C) was monitored by direct OH detection using the Fluorescence Assay by Gas Expansion (FAGE) technique.

Figure 1 shows product yields in the first temperature dependent study of the $CH_3C(O)O_2 + HO_2$ reaction. Preliminary results show significant OH yields compared to control experiments. Further modelling and data analysis is required to determine the branching ratio of the reaction which will be presented.

References

(1) H. Niki *et al.*, *J. Phys. Chem.*, **1985**, 89, 588
(2) M. E. Jenkin *et al.*, *Phys. Chem. Chem. Phys.*, **2007**, 9, 3149-3162



Fig. 1: Acetic Acid, peracetic acid, ozone and OH yields for $CH_3C(O)O_2 + HO_2$ at 760 Torr and 325 K.