Temperature Dependence of the Rate Constant and Product Studies for BrO with CH$_3$O$_2$ using a Turbulent Flow Tube coupled to Chemical Ionisation Mass Spectrometry
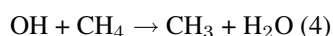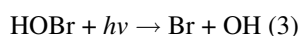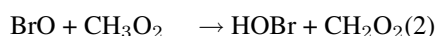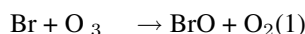
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The importance of halogen chemistry in the atmosphere and its contribution to ozone depletion is widely recognised (Farman et al. 1985; Lary and Toumi, 1997). Bromine plays a major role in catalytic cycles leading to the destruction of ozone (Salawitch, 2009; Yang, 2005) not only in the stratosphere (Anderson et al., 1991) but also parts of the troposphere, in particular the marine boundary layer (Saiz-Lopez et al., (2006) as exemplified by the catalytic cycle below.

Br + O$_3$ $\rightarrow$ BrO + O$_2$ (1)

BrO + CH$_3$O$_2$ $\rightarrow$ HOBr + CH$_2$O$_2$ (2)

HOBr + hv $\rightarrow$ Br + OH (3)

OH + CH$_4$ $\rightarrow$ CH$_3$ + H$_2$O (4)

CH$_3$ + O$_2$ $\rightarrow$ CH$_3$O$_2$ (5)

Net: CH$_4$ + O$_3$ $\rightarrow$ CH$_2$O$_2$ + H$_2$O (6)
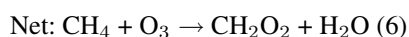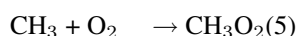
Satellite measurements of BrO have been taken in northern and southern hemispheres (Simpson et al., 2007 and references therein). Gas-phase kinetic data exist for reaction of XO (BrO, ClO, IO) with O$_3$, NO$_x$ and HO$_x$ though there are limited data concerning the reaction of XO with CH$_3$O$_2$. In order to improve modelling of halogen related chemical processes leading to ozone depletion, the determination of reaction rates and product branching ratios is essential. Since the fates of BrO are not yet fully understood, a turbulent flow chemical ionisation mass spectrometer (CIMS) shall be employed to study the kinetics and product yields of the BrO + CH$_3$O$_2$ pathway. Experiments will be conducted for reaction (2) under pseudo first order conditions using very low radical concentrations, typically $(0.5 - 20) \times 10^{10}$ molecule cm^{-3}. Rate determinations will be retrieved as a function of atmospherically relevant temperatures (T = 180 – 300 K).

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