Accelerated rate coefficients at very low temperatures: OH + ethanol

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The pulsed Laval nozzle apparatus allows the study of low temperature kinetics under thermally equilibrated conditions. This method coupled with pulsed laser photolysis laser-induced fluorescence (PLP-LIF) has been utilized to study the kinetics of the reaction between OH and ethanol under conditions approaching those of interstellar clouds where both OH and ethanol have been detected. The rate coefficient for OH + ethanol was observed to increase by over an order of magnitude between 295-80 K (Fig. 1). Similar behavior has previously been observed in our studies of OH + acetone and methanol, where a mechanism involving a weakly bound pre-reaction complex has been proposed to explain the strong inverse temperature dependence.[1]

$$\mathrm{OH} + \mathrm{C_2H_5OH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Complex} \xrightarrow{k_2} \text{Products}$$

The complex is bound by ~20 kJ mol^{-1} and is only stabilized at low temperatures. At 150 K, evidence for the role of the complex is substantiated by the observation that the reaction shows a pressure dependence (Fig. 2) which is related to the collisional stabilization of the complex. At 80 K, pressure stabilization of the complex is still evident, however a zero pressure channel is also present which implies the complex proceeds directly to products. A similar bimolecular channel has also been observed for OH + methanol and is rationalized by the occurrence of quantum mechanical tunneling from the complex through the H-abstraction barrier which has been supported theoretically by *ab inito* and MESMER calculations.[2] It is the increased lifetime of the complex at low temperatures that enhances the probability of tunneling through this barrier to products. Previous studies of OH + ethanol show that at room temperature H-abstraction occurs at the weakest bond, which is at the internal CH_2 group.[3] Surprisingly, low temperature studies of the reaction of OH + methanol have shown that quantum mechanical tunneling favours H-abstraction from the alcohol group despite the higher barrier. Enhanced quantum mechanical tunneling via this channel is a result of the higher vibrational frequency associated with breakage to the O-H bond. It is predicted that hydrogen abstraction from ethanol at low temperatures will also proceed via this channel.

References

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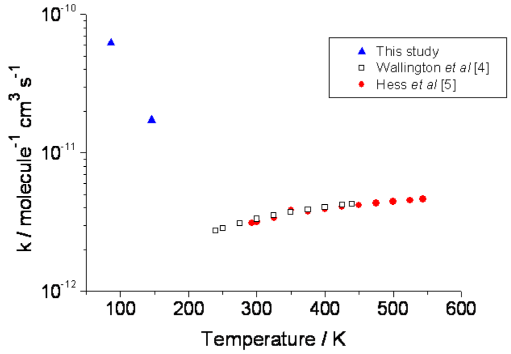
Fig. 1 : Temperature dependence of OH + ethanol

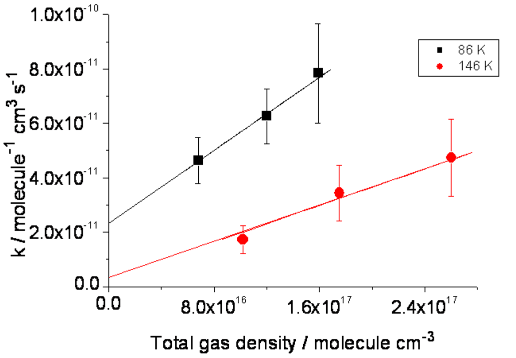
Fig. 2 : Pressure dependence of OH + ethanol