

# Accelerated Rate Coefficients at Very Low Temperatures : The Reaction of OH + Alcohols

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## 1 Introduction and Experimental Setup

- The kinetics of OH + ethanol and methanol have been studied using a pulsed Laval nozzle apparatus (Figs. 2-3) at 60-150 K over a range of pressures.
- The technique is based on the CRESU apparatus. [1,2] Room temperature reagents are expanded through the convergent-divergent Laval nozzle (Fig. 1) via two pulsed solenoid valves producing a thermally equilibrated jet due to adiabatic expansion. 60-150 K jets can be obtained using this apparatus: relevant to Titan's atmosphere and the ISM where OH, EtOH and MeOH have been detected. [3-5]
- The resultant jet from each nozzle is characterised (Table 1) using impact pressure measurements and rotationally resolved LIF spectroscopy of OH.
- Pre- and post-expansion flow pressures are related by the Rayleigh equation and the pre- and post-expansion flow temperatures and densities are calculated using the Mach number,  $M$ .

$$\frac{P_t}{P_0} = \left[ \frac{(\gamma + 1)M^2}{(\gamma - 1)M^2 + 2} \right]^{\frac{\gamma}{\gamma - 1}} \left( \frac{\gamma + 1}{2\gamma M^2 - \gamma + 1} \right)^{\frac{1}{\gamma - 1}}$$

$$\frac{T_0}{T} = 1 + \frac{\gamma - 1}{2} M^2 \quad \frac{\rho_0}{\rho} = \left( \frac{T_0}{T} \right)^{\frac{1}{\gamma - 1}}$$

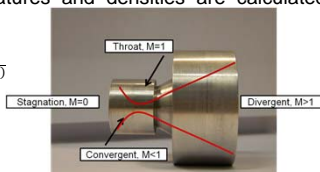


Fig. 1 : Mach numbers within the Laval nozzle

Nozzle	T / K	Gas density / molecule cm <sup>-3</sup>	Mach number
T80	86 ± 3	(6.79 ± 0.64) × 10 <sup>16</sup>	3.51 ± 0.09
	84 ± 4	(1.20 ± 0.15) × 10 <sup>17</sup>	3.57 ± 0.12
	82 ± 3	(1.59 ± 0.16) × 10 <sup>17</sup>	3.65 ± 0.10
T150	146 ± 4	(1.02 ± 0.08) × 10 <sup>17</sup>	2.26 ± 0.07
	143 ± 6	(1.75 ± 0.17) × 10 <sup>17</sup>	2.32 ± 0.09
	146 ± 8	(2.60 ± 0.37) × 10 <sup>17</sup>	2.29 ± 0.12

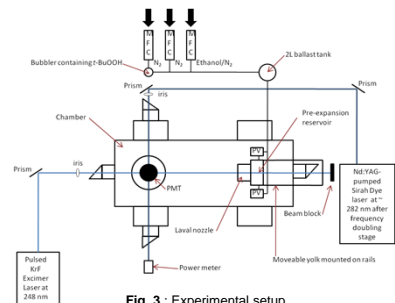


Fig. 3 : Experimental setup

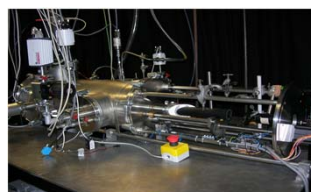


Fig. 2: University of Leeds pulsed Laval nozzle apparatus

- OH produced by excimer PLP of *t*-BuOOH at 248 nm.
- Temporal evolution of OH monitored using LIF at ~ 282 nm.
- Pseudo-first-order conditions used for kinetics experiments.
- N<sub>2</sub> used as the bath gas.

## 2 OH + EtOH

- OH + EtOH rate coefficient found to increase by over an order of magnitude between 295-80 K (Fig. 4).
- Mechanism involving weakly bound complex (-20 kJ.mol<sup>-1</sup>) [6] proposed to explain strong inverse temperature dependence (Fig. 6).
- Pressure dependence observed at 150 and 80 K associated with collisional stabilisation of the complex which occurs only at low temperatures (Fig. 5).
- Zero pressure channel at 80 K implies the complex also proceeds directly to products via quantum mechanical tunnelling through the H-abstraction barrier (Figs. 5-6).

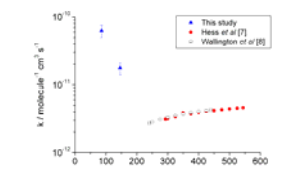


Fig. 4 : Temperature dependence of OH + ethanol

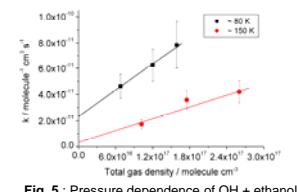


Fig. 5 : Pressure dependence of OH + ethanol

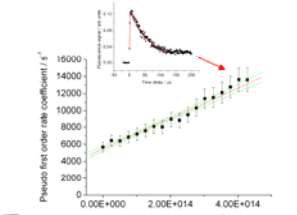


Fig. 7 : Example decay trace and bimolecular plot for OH + EtOH at 146 K,  $1.02 \times 10^{17}$  molecule cm<sup>-3</sup>,  $k = (1.79 \pm 0.35) \times 10^{-11}$  molecule<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup>

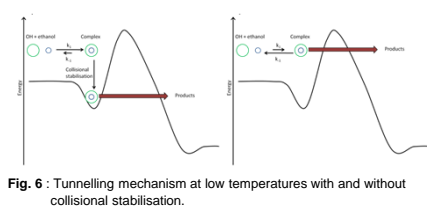


Fig. 6 : Tunnelling mechanism at low temperatures with and without collisional stabilisation.

## 4 Conclusions and Further Work

- Strong inverse temperature dependence at low temperatures observed for OH + EtOH and MeOH despite barrier to reaction.
- Accelerated rate coefficients attributed to the increased role of quantum mechanical tunnelling at low temperatures.
- Pressure dependence observed for OH + EtOH which is not seen at higher temperatures : indicating the stabilisation of a weakly bound complex between OH and EtOH.
- Bimolecular plot curvature specific to OH + MeOH reaction at 150 K: more work will be undertaken to understand this behaviour.
- Reactions of OH + EtOH at 60 K, OH + acetone at 150 K and OH + propanol will be studied in the near future.

## 5 References

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## 3 OH + MeOH

- OH + MeOH reaction greatly accelerated at low temperatures with a 72 fold increase in the rate coefficient from 210-63 (Fig. 8).
- H-bonded complex is formed which then undergoes quantum mechanical tunnelling through the H-abstraction barrier to form products.
- No pressure dependence on the rate coefficient observed (Fig. 9) indicating that there is no collisional stabilisation of the complex and so reactant removal occurs via the quantum mechanical tunnelling mechanism only.
- Master equation calculations (including tunnelling) using a PES based on that by Xu and Lin [12] and MESMER [9] predict that the predominant product of the reaction at 298 K will be CH<sub>2</sub>OH (lowest barrier pathway) – in agreement with experiment. [13]
- Master equation calculations also predict that CH<sub>3</sub>O will be produced with a branching ratio of 0.99 at 70 K.
- This mechanism is substantiated by the observation of the production of CH<sub>3</sub>O using LIF at a rate consistent with OH decay (Fig. 10).
- Reaction also studied at ~150 K. Notable curvature was observed in the bimolecular plots at low and middle flow densities – this was reduced at the highest stable density indicating a pressure-dependent process could be responsible (Fig. 11).
- Contribution of the precursor was assessed by lowering the [*t*-BuOOH] and using acetone/O<sub>2</sub> as the source of OH both of which did not reduce the curvature.
- OH + ethene used as a test reaction yielding a straight bimolecular plot (Fig. 12) and a rate coefficient consistent with that predicted in the literature. [2, 14]
- Investigations into the cause of this curvature are ongoing.

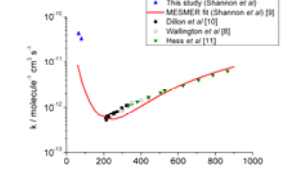


Fig. 8 : Temperature dependence of OH + methanol

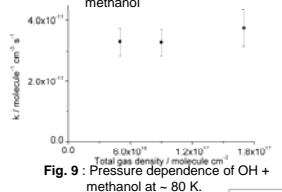


Fig. 9 : Pressure dependence of OH + methanol at ~ 80 K.

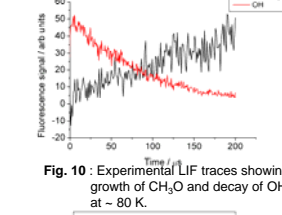


Fig. 10 : Experimental LIF traces showing growth of CH<sub>2</sub>OH and decay of OH at ~ 80 K.

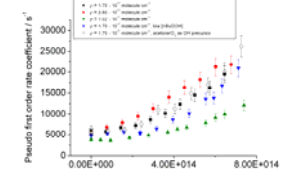


Fig. 11 : Bimolecular plot of OH + MeOH at ~ 150 K under various conditions .

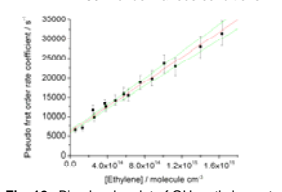


Fig. 12 : Bimolecular plot of OH + ethylene at 143 K,  $1.75 \times 10^{17}$  molecule cm<sup>-3</sup>,  $k = (1.60 \pm 0.16) \times 10^{-11}$  molecule<sup>-1</sup> cm<sup>3</sup> s<sup>-1</sup>.

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