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Measurements of Rate Coefficients for Reactions of OH with Ethanol and Propan-2-ol at Very Low Temperatures

Rebecca L. Caravan, Robin J. Shannon, Thomas Lewis, Mark A. Blitz and Dwayne E. Heard*

School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

ABSTRACT

The low temperature kinetics of the reactions of OH with ethanol and propan-2-ol have been studied using a pulsed Laval nozzle apparatus coupled with pulsed laser photolysis – laser induced fluorescence (PLP-LIF) spectroscopy. The rate coefficients for both reactions have been found to increase significantly as the temperature is lowered, by ~ a factor of 18 between 293 and 54 K for ethanol, and by ~ 10 between 298 and 88 K for OH + propan-2-ol. The pressure dependence of the rate coefficients provide evidence for two reaction channels; a zero pressure bimolecular abstraction channel leading to products and collisional stabilization of a weakly bound OH-alcohol complex. The presence of the abstraction channel at low temperatures is rationalized by a quantum mechanical tunneling mechanism, most likely through the barrier to hydrogen abstraction from the OH moiety on the alcohol.

KEYWORDS, Low temperature kinetics, astrochemistry, quantum mechanical tunneling, hydrogen-bonded complex, Laval nozzle
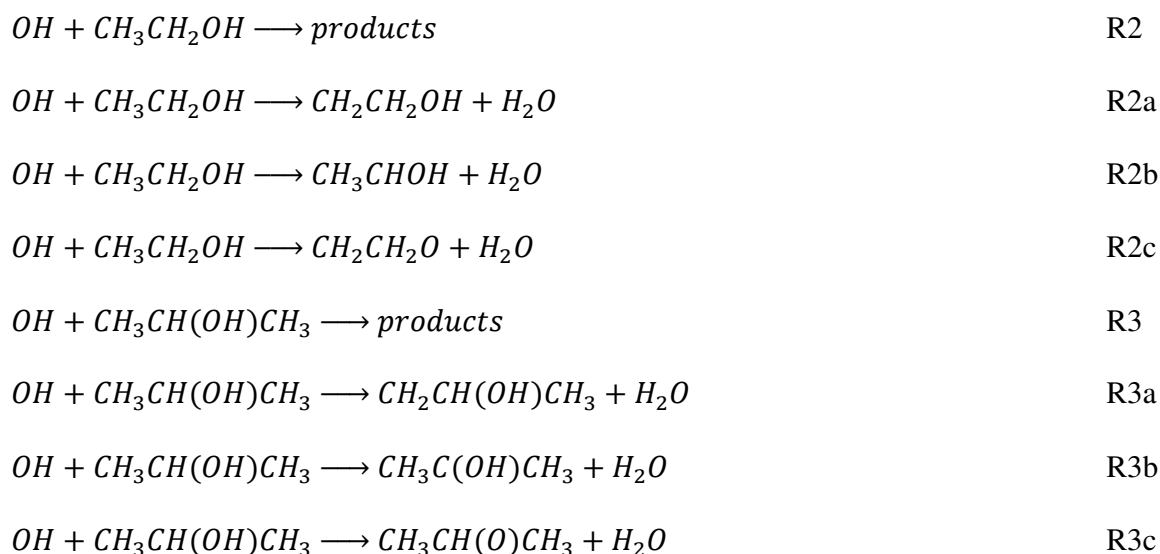
INTRODUCTION

The reactions of OH with alcohols such as ethanol and propan-2-ol have been extensively studied at ambient and high (T < 800 K) temperatures owing to their relevance to atmospheric and combustion chemistry, and more specifically, the investigation of ethanol as a potential biofuel. [1-6] In addition, both ethanol and OH have been detected in interstellar molecular clouds and star forming regions (hot and cold cores) such as W3(OH) and Sgr B2, where temperatures can reach as low as 40 K.[7-13] Millar et al.[12] suggested that ethanol could potentially be used as a chemical clock for hot cores if the kinetics of its reactions with species including the hydroxyl radical were better understood at temperatures pertinent to such environments. Conducting kinetic studies with species known to be present in these cold environments is important for the advancement of chemical models of these regions. However, recent low temperature studies of neutral-neutral reactions have shown that the temperature dependence of their rate coefficients is often complex and poorly understood, and so kinetic data close to ambient temperatures cannot simply be extrapolated.[14-17]

From previous studies it is acknowledged that at temperatures above 200 K, the reactions of OH with alcohols appear to proceed via a direct, bimolecular hydrogen abstraction mechanism (R1). [2,6,17,18]

$$OH + ROH \longrightarrow products \qquad\qquad\qquad R1$$

Such reactions exhibit parallel product channels depending on the moiety from which hydrogen abstraction occurs. For the reactions of OH with ethanol or propan-2-ol, there are three possible channels:

$$OH + CH_3CH_2OH \longrightarrow products \hspace{4cm} R2$$

$$OH + CH_3CH_2OH \longrightarrow CH_2CH_2OH + H_2O \hspace{2cm} R2a$$

$$OH + CH_3CH_2OH \longrightarrow CH_3CHOH + H_2O \hspace{2cm} R2b$$

$$OH + CH_3CH_2OH \longrightarrow CH_2CH_2O + H_2O \hspace{2cm} R2c$$

$$OH + CH_3CH(OH)CH_3 \longrightarrow products \hspace{3cm} R3$$

$$OH + CH_3CH(OH)CH_3 \longrightarrow CH_2CH(OH)CH_3 + H_2O \hspace{1cm} R3a$$

$$OH + CH_3CH(OH)CH_3 \longrightarrow CH_3C(OH)CH_3 + H_2O \hspace{1cm} R3b$$

$$OH + CH_3CH(OH)CH_3 \longrightarrow CH_3CH(O)CH_3 + H_2O \hspace{1cm} R3c$$

Extensive studies of deuterated analogues of OH + ethanol by Carr et al. have revealed that at ambient and high temperatures, abstraction from the methylene centre (R2b) is the dominant pathway.[6] Theoretical studies on this system have shown that this pathway has the lowest barrier to hydrogen abstraction and R2c has the highest.[18-21]

Kinetic studies of the reaction of OH with various deueterated analogues of propan-2-ol were performed by Dunlop and Tully between 293-502 K.[4] Analysis of the observed kinetic isotope effects demonstrated that abstraction of the alpha hydrogen (R3b) dominated, but with a significant contribution from the beta abstraction channel (R3a) that increases with temperature. *Ab initio* stationary point calculations by Galano et al. on this system showed that abstraction from the CH group (R3b) is barrierless, whereas channels R3a and R3c exhibited barriers, which is in agreement with the experimental observations by Dunlop and Tully.[20] Whilst the overall bimolecular rate coefficient for the OH + propanol reaction exhibits little dependence on temperature, which is supportive of the reaction proceeding largely via a barrierless pathway, the rate coefficient is around two orders of magnitude below the gas kinetic limit across the

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temperature range at which this reaction has until now been studied, indicating that channels with positive barriers are also contributing to the overall rate coefficient, as substantiated by the deuterated work of Dunlop and Tully.

Recent low temperature kinetic studies performed in this laboratory on the reaction of OH with methanol have shown that, unusually, the rate coefficient increases by a factor of 56 between 298 and 56 K despite the presence of barriers (9.2 and 16.5 kJ mol^{-1}) to abstraction upon the potential energy surface (PES) to form CH_2OH and CH_3O, respectively.[17,22] At low temperatures, the reaction leads to the formation of water vapor and the methoxy radical (CH_3O) as products.[17] The increase in the rate coefficient is attributed to quantum mechanical tunneling through the barrier to hydrogen abstraction, a mechanism which has also been observed in the reactions of OH with dimethyl ether and acetone, [15] and is expected to be applicable to reactions of OH with other oxygenated VOC reactions at very low temperatures. It is notable that the observed low temperature product of the OH reaction with methanol predicted by master equation modeling was not CH_2OH, which would be obtained via tunneling through the lowest energy pathway. [17]

In this paper we report the results of a kinetics study of the reactions of OH with ethanol and with propan-2-ol in the range 54 to 148 K using a pulsed Laval nozzle apparatus, and discuss the possible mechanisms to explain the observed temperature and pressure dependencies of the rate coefficients.
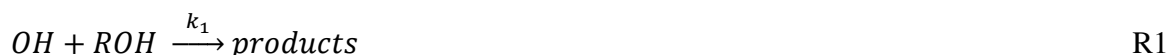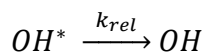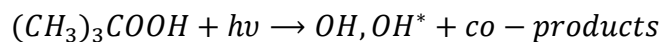
EXPERIMENTAL

The apparatus and experimental procedure has been described in detail previously and thus only a brief outline is given here.[15,23] The mixture of reagent and bath gases is expanded supersonically in ~ 10-20 ms pulses, depending on the nozzle used, through the convergent-

divergent shaped Laval nozzle into a low pressure stainless steel chamber producing a thermally equilibrated, low temperature jet. The temperature and density of the jet are characterized by impact pressure measurements and the temperature also by rotationally-resolved laser-induced fluorescence spectroscopy. The short gas pulses are achieved using two pulsed solenoid valves (Parker 9 series) which control the flow of gas from a 1 cm^3 reservoir region through the Laval nozzle. The properties of the characterized expansions used in this study alongside the experimental results, are given in Table 1.

The rate coefficients of the OH + ethanol or OH + propan-2-ol reaction are measured by monitoring the temporal decay of the hydroxyl radical via pulsed laser photolysis-laser induced fluorescence (PLP-LIF). The experiments are performed under pseudo-first-order conditions so that the concentration of the co-reagent is in great excess of the OH concentration. The OH precursor ($(CH_3)_3COOH$) is photolysed at 248 nm using an excimer laser (KrF Lambda Physik LPX 200, typical power 60-160 mJ / pulse) along the axis of the expanded gas flow producing a uniform OH density. The subsequent decay of OH due to reaction and other loss processes is measured by probing the $A^2\Sigma^+ \leftarrow X^2\Pi_i$ (1,0) Q1(1.5) transition at ~ 282 nm using a Nd:YAG (Litron LPY 664-10) pumped dye laser (Sirah Gmbh Cobra stretch with Rhodamine 6G dye). The off-resonant fluorescence at ~ 308 nm was imaged using two lenses and monitored using a photomultiplier tube (Thorn EMI) fitted with a 308 nm interference filter (Barr associates $\lambda_{max} =$ 308.5 nm, FWHM = 5 nm) positioned above the axis of the jet and laser beams. The temporal evolution of the OH radicals is recorded by varying the time delay between the photolysis and probe lasers. At very short times following photolysis, probe laser excitation scans revealed the presence of rotationally excited OH, which rapidly relaxes to the temperature of the jet obtained independently by impact pressure measurements.

The reaction scheme for the formation and removal of OH is given by:

$$(CH_3)_3COOH + hv \longrightarrow OH, OH^* + co - products$$

$$OH^* \xrightarrow{k_{rel}} OH$$

$$OH + ROH \xrightarrow{k_1} products \qquad\qquad\qquad\qquad R1$$

where OH^* is an initially rotationally excited hydroxyl radical, formed in v″=0 from photolysis of the precursor, and k_{rel} is the rate coefficient for rotational relaxation of the rotationally excited hydroxyl radical into the laser-probed level, OH. For pseudo-first-order conditions $[ROH] \gg [OH]$ the temporal evolution of OH is given:

$$[OH]_t = \left(\frac{k_{rel}}{k_{obs}-k_{rel}}\right)[OH^*]_0(e^{-k_{rel}t} - e^{-k_{obs}t}) + [OH]_0 e^{-k_{obs}t} \qquad\qquad E1$$

and

$$k_{obs} = k_1[ROH] + k_{loss} \qquad\qquad\qquad\qquad E2$$

where k_{obs} is the pseudo-first-order rate coefficient and k_{loss} is the rate coefficient for the loss of OH out of the fluorescence detection region via diffusion and reaction with the peroxide precursor. $[OH]_t$ is obtained using a standard integrating factor method assuming that the photolytic production of OH and OH^* is instantaneous, and that rotational relaxation is much faster than the reaction with ROH. If a single exponential decay expression, corresponding to the second term in equation E1 only, is fitted to the data for later delay times following the initial

fast growth of OH, then a very similar value of k_{obs} is obtained, and well within the error of the returned value.

The vapor pressure of the alcohol (ethanol (Sigma-Aldrich, ethanol absolute $\geq$ 99.8 %) or propan-2-ol (Fischer scientific, 99.5 %)) was admitted to an evacuated cylinder, then diluted with nitrogen (BOC, OFN) or argon (99.998 %, BOC) and allowed to mix overnight – the concentration of the alcohol in the cylinders was determined by pressure measurements. The alcohol/bath gas mixture, $(CH_3)_3COOH$ (Aldrich, 70 % wt. in H_2O) and the bath gas (nitrogen (BOC, OFN) or argon (99.998 %, BOC)) were delivered to the pre-expansion reservoir via a set of calibrated mass flow controllers (MKS instruments). $(CH_3)_3COOH$ was seeded in a flow of nitrogen (OFN) via a glass bubbler. All experiments were carried out under pseudo-first-order conditions and in addition the reagent concentration did not exceed 2 % of the total gas flow.

RESULTS

Examples of the temporal evolution of the OH LIF signal following 248 nm photolysis of $(CH_3)_3COOH$ in the presence of ethanol and propan-2-ol are shown in Figure 1, together with non-linear least squares fits of (E1) to the data which yielded k_{obs}. Experiments were repeated for a variety of concentrations of either ethanol or propan-2-ol, and Figure 2 shows the variation of k_{obs} with [alcohol], the gradients of which yield the bimolecular rate coefficients. The rate coefficients obtained in this study are summarized in Table 1, and the temperature dependence of $k_{OH + ethanol}$ and $k_{OH + propan-2-ol}$ are shown in Figure 3. The rate coefficient for the reaction of OH + ethanol measured at 56 K is found to be a factor of 18 higher than the value reported at 293 K by Hess and Tully,[24] signifying a strong inverse temperature dependence at lower temperatures. The

rate coefficient for OH + propan-2-ol is also found to exhibit a notable inverse temperature dependence below 240 K, as shown in Figure 1(b), increasing by around an order of magnitude between 296 and 88 K.[5] The rate coefficients $k_{\text{OH + ethanol}}$ and $k_{\text{OH + propan-2-ol}}$ were measured over a range of total bath gas densities and, in contrast to the reaction of OH with methanol,[17] the measured rate coefficients demonstrate a pressure dependence at the low temperatures studied in this work, as shown in Figure 4.

DISCUSSION

Figure 5 shows the generic potential energy surface of the reaction of OH with ethanol or propan-2-ol, based on calculations reported in the literature, from which it can be seen that a weakly bound complex (between ~18-27 kJmol^{-1}) is formed prior to any barrier to abstraction.[18-20]. The overall reaction (R1) can be described by an extended-Hinshelwood type mechanism:

$$OH + ROH \xrightarrow{k_a} [complex]^* \qquad \text{R1a}$$

$$[complex]^* \xrightarrow{k_{-a}} OH + ROH \qquad \text{R1b}$$

$$[complex]^* + M \xrightarrow{k_s} [complex] + M \qquad \text{R1c}$$

$$[complex]^* \xrightarrow{k_r} products \qquad \text{R1d}$$

The enhancement in the rate coefficient k_1 with total gas density shown in Figure 4 is a result of the increasing collisional stabilization of the complex. From this scheme, the rate of change of OH and the complex are given by:

$$\frac{-d[OH]}{dt} = k_a[OH][ROH] - k_{-a}[complex]^* \qquad \text{E3}$$

$$\frac{d[complex]^*}{dt} = k_a[OH][ROH] - k_{-a}[complex]^* - k_s[M][complex]^* - k_r[complex]^*. \qquad \text{E4}$$

Applying the steady state approximation to the complex gives:

$$[complex]^* = \frac{k_a\,[OH][ROH]}{k_{-a}+k_s[M]+k_r} \qquad \text{E5}$$

and hence:

$$\frac{-d[OH]}{dt} = \left(k_a - \frac{k_{-a}k_a}{k_{-a}+k_s[M]+k_r}\right)[OH][ROH] \qquad \text{E6}$$

The experimental rate law for the loss of OH via reaction with ROH is defined by;

$$\frac{-d[OH]}{dt} = k_1[OH][ROH] \qquad \text{E7}$$

and comparing terms with E6 leads to:

$$k_1 = \frac{k_a\,(k_{-a}+k_s[M]+k_r)}{k_{-a}+k_s[M]+k_r} - \frac{k_{-a}k_a}{k_{-a}+k_s[M]+k_r} = \frac{k_a\,k_s[M]}{k_{-a}+k_s[M]+k_r} + \frac{k_a\,k_r}{k_{-a}+k_s[M]+k_r}$$

which is equivalent to:

$$k_1 = \frac{[M]}{\frac{k_{-a}}{k_a\,k_s}+\frac{[M]}{k_a}+\frac{k_r}{k_a\,k_s}} + \frac{1}{\frac{k_{-a}}{k_a\,k_r}+\frac{k_s[M]}{k_a\,k_r}+\frac{1}{k_a}} \qquad \text{E8}$$

The expression E8 enables the Lindemann-Hinshelwood parameters to be obtained by fitting to

observations of $k_{\text{OH + ethanol}}$ or $k_{\text{OH + propan-2-ol}}$ as a function of [M], as shown in Figure 4.[25] The rate

coefficient for the pressure independent abstraction channel is given by k_1 at [M]=0 (when only

the second term in E8 remains) which is $k_1 = \dfrac{k_a k_r}{k_{-a} + k_r}$, and the ratio $\dfrac{k_r}{k_s}$ (previously referred to

as the chemical activation ratio [25]) can be obtained from the ratio of the value of k_1 at [M]=0 to

the low pressure limiting gradient of k_1 versus [M] ($\dfrac{k_a k_s}{k_{-a} + k_r}$). To deduce the chemical activation

ratio and the rate coefficient for the pressure independent abstraction channel, the high pressure

limit, $k_1 = k_a$, was fixed at values obtained experimentally at ~ 89 K using the proxy method,

first developed by Troe and Quack, and by Smith and co-workers [26,27] for pressure dependent

reactions. In the proxy method, the temporal decay of vibrationally excited OH following

collisions with the co-reagent (alcohol in our case) is monitored and used to determine the high

pressure limit. The assumption is made that following formation of the collision complex with

the alcohol, the excess vibrational energy initially in OH(v) is rapidly redistributed amongst the

many other modes of the complex, and any OH formed following dissociation of the complex is

in v=0. Monitoring OH(v">0) therefore provides a measurement of the capture rate coefficient

for complex formation, k_a. The complete results and methodology for the proxy method as

applied to low temperatures within the Laval nozzle apparatus will be reported in a forthcoming

publication. The same high pressure limiting value was used for both the ~82-91 K and ~133-

148 K data, as the barrierless association reaction which k_a represents is expected to be

relatively independent of temperature. The values of k_a used and the values of $\dfrac{k_r}{k_s}$, and

$k_1(M \rightarrow 0) = \dfrac{k_a k_r}{k_{-a} + k_r}$ obtained from the fits are displayed in Table 2.

From Figure 4 it can be seen that at low temperatures the rate coefficient extrapolated to

[M]=0 is significant, indicative of a pressure independent product channel. In the case of ethanol,

for which all product channels proceed via a significant activation barrier, this provides evidence

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for quantum mechanical tunneling, as observed for methanol.[17] For propan-2-ol, although the abstraction channel R3b is calculated to be barrierless[20], and hence could proceed at very low temperatures, the rate coefficient between 250 – 750 K is only ~ 5×10^{-12} cm^3 molecule^{-1} s^{-1} (see Figure 3) and relatively independent of temperature, whereas as shown in Figure 4, the intercept at [M] =0 for 89 K gives a value that is almost 10 times higher. This finding provides evidence for a further mechanism that is operating at very low temperatures, namely the formation of a longer-lived complex which facilitates quantum mechanical tunneling, as observed for OH+methanol.[17]

As [M] increases, this pressure independent contribution to k_1 becomes less significant and the first term in E8 begins to dominate, representing the collisional stabilization of the hydrogen-bonded OH-alcohol complex. Figure 6 shows the best-fit of the extended Lindemann-Hinshelwood expression E8 to pressure dependent data for the reaction of OH with ethanol at 82-89 K (as shown in Figure 4), together with the individual contributions towards k_1 of the two right-hand-side terms of E8 as a function of pressure. Using the mechanism above, in the limit of low pressure, k_1 ([M]$\rightarrow$0) = $\dfrac{k_a k_r}{k_{-a} + k_r}$, and when there is a barrier to forming products, k_r, and hence k_1 will be small, even though k_{-a} will decrease significantly at low temperatures. However, when quantum mechanical tunneling is significant (for example in hydrogen transfer reactions such as these), the value of k_r is significant and hence at low temperatures the value of k_1 can increase significantly. The pressure independent rate coefficient, estimated by fitting E8 to the experimental data as shown in Figure 4, is significantly larger at ~ 82-89 K for ethanol compared with ~ 133-148 K, consistent with this mechanism. Although at ~54-56 K there are only two data points which overlap within experimental uncertainties, there is evidence for a larger pressure independent rate coefficient.

At high temperatures where there is sufficient energy to surmount the barrier to reaction, there is rapid formation (R1a) and dissociation (R1b) of the complex and so the bottleneck for reaction (R1d) is location at the barrier itself. The complex has a short lifetime and collisional stabilization is not able to compete with dissociation, and consequently only the pressure independent abstraction channel (R1d) is observed. Only at low temperatures is k_{-a} sufficiently reduced such that the lifetime of the complex is long enough for collisional stabilization to compete with dissociation. [15,28,29] The magnitude of the pressure independent, bimolecular rate coefficient (the intercepts of Figures 4(a) and (b)) increases gradually towards the gas kinetic limit for this reaction as the temperature is lowered. However, as the temperature is lowered, the complex can also be collisionally stabilized into the pre-barrier well, and this stabilization channel is competitive with the bimolecular channel. As the pressure is increased, the role of collisional stabilization becomes more important, whereas that of the bimolecular channel diminishes, as illustrated in Figure 6.

In the case of OH + propan-2-ol, the bimolecular abstraction reaction can occur via a submerged barrier for channel R3b.[20] The observed increase in the rate coefficient for this bimolecular channel at low temperatures is due to the reduction in k_{-a} (R1b) and hence an extended complex lifetime with decreasing temperature , resulting in a higher probability of the complex proceeding to products either via the submerged barrier or by tunneling through one of the other barriers to hydrogen abstraction. Furthermore, the lifetime of the complex is sufficiently long that collisional stabilization is competitive, as evident from Figure 4 (b).

In the case of the ethanol system, there is uncertainty in the literature as to whether the lowest barrier to H-abstraction (R2b) is submerged or not. Work by Sivaramakrishnan et al.[19] at the QCISD(T)/CBS//B3LYP/6-311++G(d,p) level of theory indicates a slightly submerged or

energetically neutral barrier, with an error larger than the energy by which the barrier is submerged being placed on the value. The findings of Xu and Lin[18] using theory at the CCSD(T)/6-311+G(3df,2p) level support this. Conversely, calculations by Galano et al.[20] at the CCSD(T)/6-311G(d,p)//BHandHLYP/6-311++G(d,p) level yield a small positive barrier as indicated schematically in Figure 5. From the Arrhenius type behavior of the experimental data currently in the literature at higher temperatures, as shown in Figure 3, it is expected that this barrier is indeed positive or that the transition state is sufficiently tight so that the kinetic behavior appears as if there is a positive barrier. Considering the low temperatures at which the experiments reported here have been undertaken and its demonstrated role in the OH + methanol reaction for a similar temperature range,[17,22] the contribution of quantum mechanical tunneling in the OH + ethanol reaction (and perhaps to certain channels of the OH + propanol-2-ol reaction) must be considered.

At higher temperatures, where there is sufficient energy to surmount the barriers to reaction, the contribution from quantum mechanical tunneling is reduced and the relative heights of the barriers to hydrogen atom abstraction from the different moieties on ethanol or propan-2-ol influence the branching ratios of the products. However, at low temperatures when the quantum mechanical tunneling mechanism dominates reaction, the product branching ratios are predominantly influenced by the shape of the vibrationally adiabatic reaction path, in other words, the barrier widths.[17,30,31] Therefore, in the case of OH + ethanol it is likely that hydrogen atom abstraction process is not occurring through the lowest energy barrier, which corresponds to abstraction from the CH_2 moiety (R2b) to form CH_3CHOH, but instead through the barrier which has the largest imaginary frequency (~2300-2900 cm^{-1}), which is abstraction from the hydroxyl group (R2c) resulting in ethoxy radical formation, CH_3CH_2O.[18-20] Although this

channel has been experimentally and theoretically determined to be relatively inactive at ambient temperatures,[6,19] our previous work on the OH + methanol reaction has shown that abstraction via the barrier with the largest imaginary frequency (also the OH group, to form CH_3O) dominates at low temperatures.[17] An unsuccessful attempt has been made in this work to detect the analogous CH_3CH_2O radical product of this abstraction channel via laser-induced fluorescence spectroscopy. We postulate that the inability to observe this product is in part due to fast secondary reactions of the CH_3CH_2O radical with other radicals such as OH and H, which were abundant in the experiments where product detection was attempted, resulting in chemiluminescence which obscured the laser induced fluorescence signal.[22]

Although there is a barrierless abstraction channel for the OH + propan-2-ol reaction (R3b), quantum mechanical tunneling through the barrier associated with abstraction from the OH group of propanol-2-ol (R3c) may be competitive at low temperatures, due to the high imaginary frequency.[20] Consequently, the distribution of products at low temperatures may differ from the room temperature branching ratios. The pressure independent rate coefficients for the reactions of OH with ethanol and propan-2-ol increase by around a factor of 8 between 298 and 84 K, obtained from extrapolations of the Lindemann-Hinshelwood fits to [M]=0 and corresponding to the product formation channels. These product channels are of potential relevance to star forming regions and molecular clouds in the interstellar medium as the low gas density ($\sim 10^2$-10^4 molecule cm^{-3}) in these environments means that collisions are very infrequent and hence collisional stabilization of the complex (R1c) is precluded.[10] For the mechanism outlined above,

k_1 ([M]$\rightarrow$0) = $\dfrac{k_a k_r}{k_{-a} + k_r}$ and hence at the very low temperatures present in these regions, when k_{-a}

$\rightarrow$ 0, k_1 = k_a and the bimolecular reaction to form products will be encounter controlled and

approach the gas kinetic limit. Hence reactions of this type, involving the formation of pre-barrier hydrogen-bonded complexes, may be important in these interstellar environments.

CONCLUSIONS

Rate coefficients for the reaction of OH with ethanol and propan-2-ol were observed to increase significantly at very low temperatures, and measurements of the rate coefficients across a range of pressures enabled demonstration of a significant reaction occurring at zero-pressure. These results support our previous work on reactions of OH with oxygenated VOCs, and provide further evidence for a mechanism involving the formation of a weakly bound hydrogen-bonded complex, the lifetime of which is significantly extended at low temperatures, increasing the rate coefficient. [14,17,22] Furthermore, the formation of the longer-lived complex at low temperature enhances the probability of hydrogen atom transfer via quantum mechanical tunneling to form products. It is postulated that this mechanism may be general for reactions of OH with oxygenated volatile compounds, and that these reactions should be considered in networks describing the chemistry of the interstellar medium. Further theoretical work is required to calculate the low temperature rate coefficients and product branching ratios of these types of reactions.

AUTHOR INFORMATION

Corresponding Author

*(D.E.H.) Email: d.e.heard@leeds.ac.uk Phone number: +44 (0)113 3436471

Notes

The authors declare no competing financial interests.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

1   Wu, H., Mu, Y., Zhang, X. & Jiang, G. Relative Rate Constants for the Reactions of Hydroxyl Radicals and Chlorine Atoms with a Series of Aliphatic Alcohols. *Int. J. Chem. Kinet.* **35**, 81-87 (2003).

2   Dillon, T. J., Holscher, D., Sivakumaran, V., Horowitz, A. & Crowley, J. N. Kinetics of the Reactions of HO with Methanol (210-351 K) and with Ethanol (216-368 K). *Phys. Chem. Chem. Phys.* **7**, 349-355 (2005).

3   Jimenez, E., Gilles, M. K. & Ravishankara, A. R. Kinetics of the Reactions of the Hydroxyl Radical with CH_3OH and C_2H_5OH between 235 and 360 K. *J. Photoch. Photobio. A* **157**, 237-245 (2003).

4   Dunlop, J. R. & Tully, F. P. Catalytic Dehydration of Alcohols by Hydroxyl: 2-Propanol; An Intermediate Case. *J. Phys. Chem.* **97**, 6457-6464 (1993).

5   Wallington, T. J. & Kurylo, M. J. The Gas-Phase Reactions of Hydroxyl Radicals with a Series of Aliphatic-Alcohols over the Temperature-Range 240-440-K. *Int. J. Chem. Kinet.* **19**, 1015-1023 (1987).

6   Carr, S. A., Blitz, M. A. & Seakins, P. W. Site-Specific Rate Coefficients for Reaction of OH with Ethanol from 298 to 900 K. *J. Phys. Chem. A* **115**, 3335-3345 (2011).

7   Combes, F., Gerin, M., Wootten, A., Wlodarkczak, G., Clausset, F., Encrenaz, P.J. Acetone in Interstellar Space. *Astron Astrophys.* **180**, L13 - L16 (1987).

8   Ohishi, M. in *Molecules in Astrophysics : Probes and Processes. Proceedings of the 178th Symposium of the International Astronomical Union, held in Leiden, The Netherlands, July 1-5, 1996.* (ed E. F. van Dishoeck) (Kluwer Academic Publishers, 1996).

9   Thi, W.-F., van Zadelhoff, G.-J. & van Dishoeck, E. F. Organic Molecules in Protoplanetary Disks Around T Tauri and Herbig Ae Stars. *Astron. Astrophys.* **425**, 955-972 (2004).

10 van Dishoeck, E. F., Blake, G. A., Draine, B. T. & Lunine, J. I. in *Protostars and planets* Vol. III (A93-42937 17-90) 163-241 (1993).

11 Robinson, B. J. & McGee, R. X. OH Molecules in the Interestellar Medium. *Ann. Rev. Astron. Astr.* **5**, 183-212 (1967).

12 Millar, T. J., Macdonald, G. H. & Habing, R. J. The Detection of Hot Ethanol in G34.3+0.15. *Mon Not R Astron Soc* **273**, 25-29 (1995).

13 Smith, I. W. M., Sage, A. M., Donahue, N. M., Herbst, E. & Quan, D. The Temperature-Dependence of Rapid Low Temperature Reactions: Experiment, Understanding and Prediction. *Faraday Discuss.* **133**, 137-156 (2006).

14 Shannon, R. J., Taylor, S., Goddard, A., Blitz, M. A. & Heard, D. E. Observation of a Large Negative Temperature Dependence for Rate Coefficients of Reactions of OH with Oxygenated Volatile Organic Compounds Studied at 86-112 K. *Phys. Chem. Chem. Phys.* **12**, 13511-13514 (2010).

15 Shannon, R. J., Caravan, R. L., Blitz, M. A. & Heard, D. E. A Combined Experimental and Theoretical Study of Reactions between the Hydroxyl Radical and Oxygenated Hydrocarbons Relevant to Astrochemical Environments. *Phys. Chem. Chem. Phys.* **16**, 3466-3478 (2014).

16 Tizniti, M. *et al.* The Rate of the $F + H_2$ Reaction at Very Low Temperatures. *Nature Chem.* **6**, 141-145 (2014).

17   Shannon, R. J., Blitz, M. A., Goddard, A. & Heard, D. E. Accelerated Chemistry in the Reaction between the Hydroxyl Radical and Methanol at Interstellar Temperatures Facilitated by Tunnelling. *Nature Chem.* **5**, 745-749 (2013).

18   Xu, S. & Lin, M. C. Theoretical Study on the Kinetics for OH Reactions with CH_3OH and C_2H_5OH. *P. Combust. Inst.* **31**, 159-166 (2007).

19   Sivaramakrishnan, R. *et al.* Rate Constants for the Thermal Decomposition of Ethanol and Its Bimolecular Reactions with OH and D: Reflected Shock Tube and Theoretical Studies. *J. Phys. Chem. A* **114**, 9425-9439 (2010).

20   Galano, A., Alvarez-Idaboy, J. R., Bravo-Pérez, G. & Ruiz-Santoyo, M. E. Gas Phase Reactions of C1–C4 Alcohols with the OH Radical: A Quantum Mechanical Approach. *Phys. Chem. Chem. Phys.* **4**, 4648-4662 (2002).

21   Zheng, J. & Truhlar, D. G. Multi-Path Variational Transition State Theory for Chemical Reaction Rates of Complex Polyatomic Species: Ethanol+ OH Reactions. *Faraday Discuss.* **157**, 59-88 (2012).

22   Gomez Martin, J. C., Caravan, R. L., Blitz, M. A., Heard, D. E. & Plane, J. M. C. Low Temperature Kinetics of the CH_3OH + OH Reaction. *J. Phys. Chem. A* **118**, 2693-2701 (2014).

23   Taylor, S. E., Goddard, A., Blitz, M. A., Cleary, P. A. & Heard, D. E. Pulsed Laval Nozzle Study of the Kinetics of OH with Unsaturated Hydrocarbons at Very Low Temperatures. *Phys. Chem. Chem. Phys.* **10**, 422-437 (2008).

24   Hess, W. P. & Tully, F. P. Catalytic Conversion of Alcohols to Alkenes by OH. *Chem. Phys. Lett.* **152**, 183-189 (1988).

25   Romero, M. T. B. *et al.* OH Formation from the C_2H_5CO+ O_2 Reaction: An Experimental Marker for the Propionyl Radical. *Chem. Phys. Lett.* **408**, 232-236 (2005).

26   Quack, M. & Troe, J. Complex Formation in Reactive and Inelastic Scattering: Statistical Adiabatic Channel Model of Unimolecular Processes III. *Berichte der Bunsengesellschaft für physikalische Chemie* **79**, 170-183 (1975).

27   Jaffer, D. H. & Smith, I. W. M. Time-Resolved Measurements on the Relaxation of OH(v= 1) by NO, NO_2 and O_2. *Faraday Discuss.* **67**, 212-220 (1979).

28   Greenwald, E. E., North, S. W., Georgievskii, Y. & Klippenstein, S. J. A Two Transition State Model for Radical−Molecule Reactions: A Case Study of the Addition of OH to C_2H_4. *J. Phys. Chem. A* **109**, 6031-6044 (2005).

29   Greenwald, E. E., North, S. W., Georgievskii, Y. & Klippenstein, S. J. A Two Transition State Model for Radical−Molecule Reactions: Applications to Isomeric Branching in the OH−Isoprene Reaction. *J. Phys. Chem. A* **111**, 5582-5592 (2007).

30   Bell, R. P. *The Tunnel Effect in Chemistry*. (Chapman and Hall, 1980).

31   Carpenter, B. K. Heavy-Atom Tunneling as the Dominant Pathway in a Solution-Phase Reaction? Bond Shift in Antiaromatic Annulenes. *J. Am. Chem. Soc.* **105**, 1700-1701 (1983).

32   Nelson, L. *et al.* Absolute and Relative Rate Constants for the Reactions of Hydroxyl Radicals and Chlorine Atoms with a Series of Aliphatic Alcohols and Ethers at 298 K. *Int. J. Chem. Kinet.* **22**, 1111-1126 (1990).

Table 1. Measured rate coefficients together with the temperatures and total densities of the flows generated by the pulsed Laval nozzles used in this study.

T / K	Bath gas (M)	$[M] / 10^{16}$ molecule cm^{-3}	$k_{(OH + ethanol)} / 10^{-11}$ molecule^{-1} cm^3 s^{-1}	$k_{(OH + propan-2-ol)} / 10^{-11}$ molecule^{-1} cm^3 s^{-1}
56 ± 4	Ar	4.4 ± 0.5	6.0 ± 0.5	-
54 ± 6	Ar	8 ± 1	5.5 ± 0.7	-
88 ± 5	N$_2$	3.5 ± 0.5	4.0 ± 0.6	5.5 ± 0.7
89 ± 3	N$_2$	6.5 ± 0.6	4.2 ± 0.2	5.7 ± 0.7
86 ± 3	N$_2$	6.8 ± 0.6	5 ± 2	-
91 ± 4	N$_2$	8.3 ± 0.9	-	6.7 ± 0.7
88 ± 4	N$_2$	11 ± 1	5.5 ± 0.6	7 ± 1
84 ± 4	N$_2$	12 ± 2	6 ± 2	-
82 ± 3	N$_2$	16 ± 2	7 ± 3	-
138 ± 9	N$_2$	8 ± 1	1.7 ± 0.2	3.6 ± 0.3
148 ± 15	N$_2$	10 ± 2	1.7 ± 0.4	-
133 ± 10	N$_2$	13 ± 3	3.6 ± 0.3	4.7 ± 0.4
143 ± 15	N$_2$	18 ± 2	3.6 ± 0.8	-
146 ± 15	N$_2$	26 ± 4	4 ± 1	-

Errors have been calculated by propagation of the 95 % confidence limits in the bimolecular rate coefficients with the errors in the expansion densities.

Table 2. Parameters obtained from the fit of the extended Lindemann-Hinshelwood expression (E8) to the experimental pressure dependent data.

System	T / K	High pressure limit* k_a / molecule^{-1} cm^3 s^{-1}	Chemical activation ratio $\dfrac{k_r}{k_s}$	Zero pressure rate coefficient $\dfrac{k_a k_r}{k_{-a}+k_r}$ / molecule^{-1} cm^3 s^{-1}
OH + ethanol	82-91	4.5×10^{-10}	$(1.0\pm0.8)\times10^{17}$	$(2.7\pm0.8)\times10^{-11}$
	133-148	4.5×10^{-10}	$(3.6\pm5.9)\times10^{16}$	$(6.2\pm8.1)\times10^{-12}$
OH + propan-2-ol	88-91	4.7×10^{-10}	$(1.8\pm0.7)\times10^{17}$	$(4.6\pm0.5)\times10^{-11}$

* High pressure limits obtained experimentally using the proxy method of monitoring the decay of vibrationally excited OH, the details of which will be presented in a forthcoming publication.
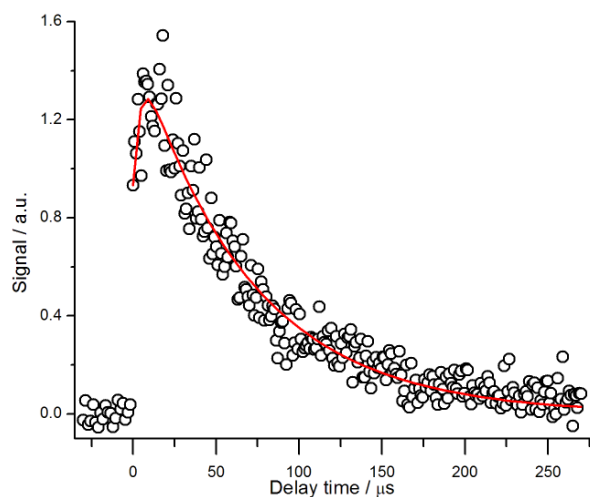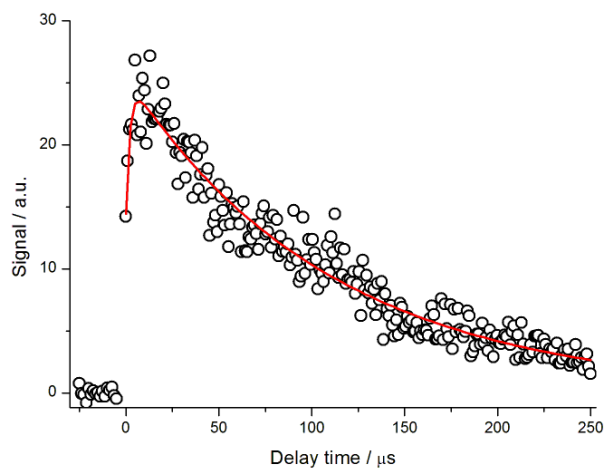
Figure 1: Temporal evolution of the OH LIF signal (black open circles) together with non-linear least-squares fits of equation (E1) to the data (red lines) following 248 nm photolysis of $(CH_3)_3COOH$ in the presence of (Upper panel), [ethanol] = 8.4×10^{13} molecule cm^{-3}, total density $(4.4 \pm 0.5) \times 10^{16}$ molecule cm^{-3} in Ar, T = 56 ± 4 K, fit gives $k_{obs} = 9342 \pm 181$ s^{-1} and (Lower panel) [propan-2-ol] = 1.2×10^{14} molecule cm^{-3}, T = 91 ± 4 K, total density = $(8.3 \pm 0.9) \times 10^{16}$ molecule cm^{-3} in N_2, fit gives $k_{obs} = 14767 \pm 347$ s^{-1}.
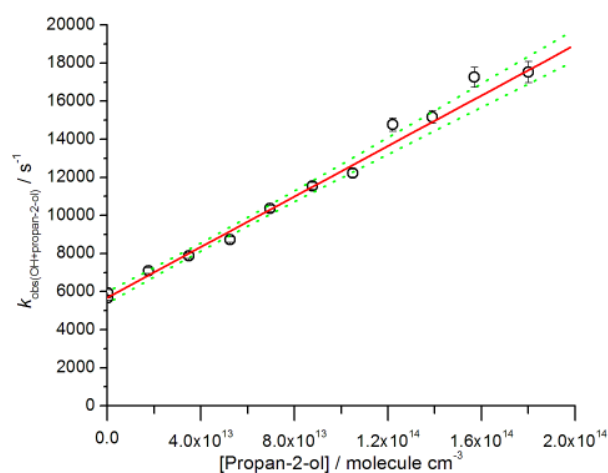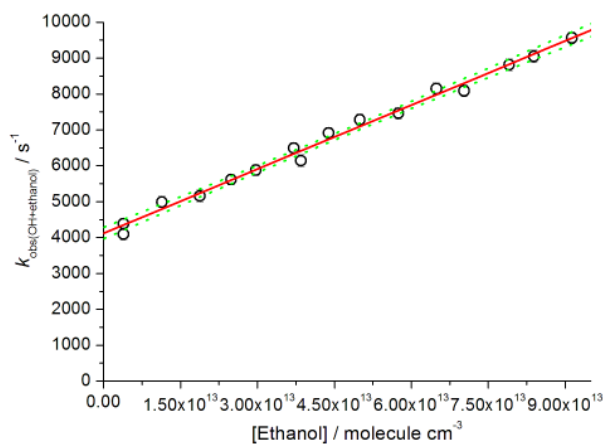
Figure 2. Variation of k_{obs} with alcohol concentration (black open circles), together with a weighted linear least-squares fits of equation (E2) to the data (red lines), the gradient of which yields the bimolecular rate coefficient. The green dashed lines represent the upper and lower 95 % confidence limits. (Upper panel) OH reaction with ethanol, T = 56 ± 4 K, density = (4.4 ± 0.5)×10^{16} molecule cm^{-3}, gradient gives $k_{OH + ethanol}$ = (6.0 ± 0.5) × 10^{-11} molecule^{-1} cm^{3} s^{-1}. (Lower panel) OH reaction with propan-2-ol, T = 91 ± 4 K, density = (8.3 ± 0.9) × 10^{16} molecule cm^{-3}, gradient yields $k_{OH + propan-2-ol}$ = (6.7 ± 0.7) × 10^{-11} molecule^{-1} cm^{3} s^{-1}. The overall error in k is the 95 % confidence limits on the gradient propagated with the error in the determination of the total density. .
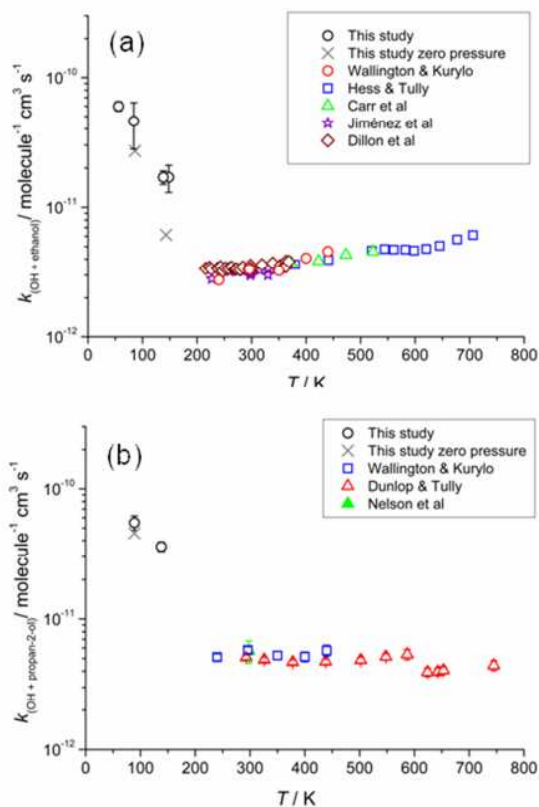
Figure 3. (a) Temperature dependence of the rate coefficient for OH + ethanol. Red open circles: Wallington and Kurylo.[5] Blue open squares: Hess and Tully.[24] Green open triangles: Carr et al.[6] Purple open stars: Jiménez et al.[3] Dark red open diamonds: Dillon et al.[2] Black open circles: This study. Values shown are for 56 ± 4 K (total density of bath gas $(4.4 ± 0.5) × 10^{16}$ molecule cm^{-3} in Ar), 88 ± 5 K $((3.5 ± 0.5) × 10^{16}$ molecule cm^{-3} in N_2), 138 ± 9 K $((8 ± 1) × 10^{16}$ molecule cm^{-3} in N_2) and 148 ± 15 K $((1.0 ± 0.2) × 10^{17}$ molecule cm^{-3} in N_2). Grey crosses: This study, zero pressure rate coefficient from intercept of fit of extended Lindemann-Hinshelwood expression (E8) to the experimental data. **(b)** Temperature dependence of the rate coefficient for OH + propan-2-ol. Blue open squares: Wallington and Kurylo.[5] Red open triangles: Dunlop and Tully.[4] Green closed triangle: Nelson et al.[32] Black open circles: This study. Values shown are for 88 ± 5 K $((3.5 ± 0.5) × 10^{16}$ molecule cm^{-3} in N_2) and 138 ± 9 K $((8 ± 1) × 10^{16}$ molecule cm^{-3} in N_2). Grey crosses: This study, zero pressure rate coefficient from intercept of fit of extended Lindemann-Hinshelwood expression (E8) to the experimental data.
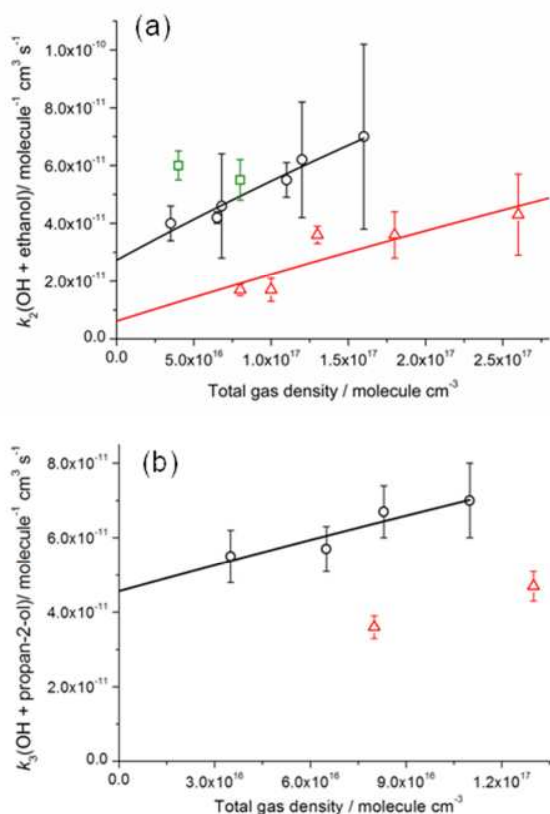
Figure 4. (a) Pressure dependence of the rate coefficient for OH + ethanol at 54-56 K (green open squares, Ar bath gas), 82-89 K (black open circles, N_2 bath gas) and 133-148 K (red open triangles N_2 bath gas). All values of the temperatures, densities and rate coefficients are given in Table 1. The black and red lines are the extended Lindemann-Hinshelwood fits (E8) to the data at 82-89 K and 133-148 K respectively. See text for details. Error bars represent propagation of the 95 % confidence limits (including the whole covariance matrix) in the bimolecular rate coefficients with the errors in the expansion densities. **(b)** Pressure dependence of the rate coefficient for OH + propan-2-ol at 89 K (black open circles) and 133-138 K (red open triangles). The black line is the extended Lindemann-Hinshelwood fit (E8) to the data at 89 K. Error bars as for (a).
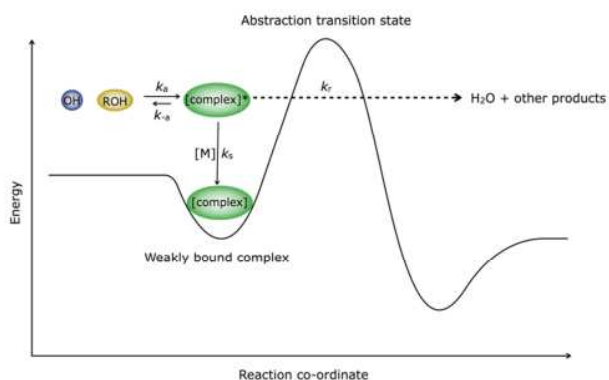
Figure 5. Generic potential energy surface for an OH + alcohol reaction illustrating the possible reaction pathways occurring. k_s is the rate coefficient for the collisional stabilization of the hydrogen-bonded complex and k_r is the rate coefficient for the formation of products.
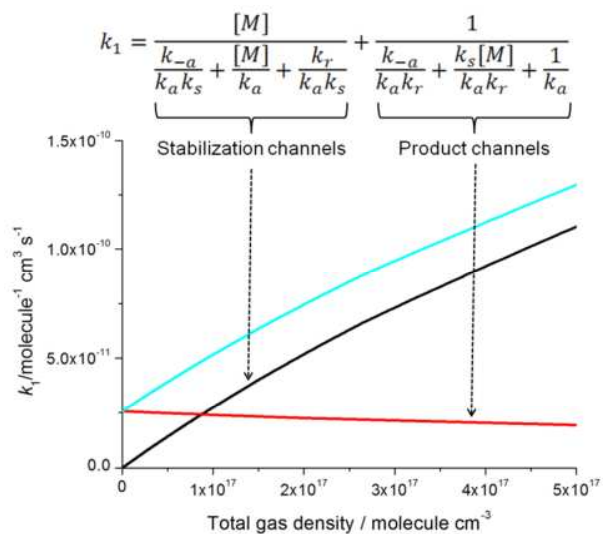
Figure 6. The extended Lindemann-Hinshelwood expression (E8) for k_1 as a function of [M] using the best-fit parameters from fitting to the 82-89 K OH + ethanol experimental data (cyan line), together with the calculated contributions to k_1 from the pressure dependent first term (black line) and the approximately pressure independent second term (red line) as a function of total gas density.