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Accelerated chemistry in the reaction of OH with methanol at interstellar temperatures facilitated by tunnelling

Robin J. Shannon[1], Mark. A. Blitz[1,2], Andrew Goddard[1] and Dwayne E. Heard[1,2*]

[1] *School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK*
[2] *National Centre for Atmospheric Science, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK*
[*] e-mail: d.e.heard@leeds.ac.uk

Understanding the abundances of molecules observed in dense interstellar clouds requires knowledge of the rates of gas phase reactions between two neutral species. However, reactions possessing an activation barrier were considered too slow to play any important role at the low temperatures in these clouds. Here we show that despite the presence of a barrier the rate coefficient for the reaction between the hydroxyl radical (OH) and methanol, one of the most abundant organic molecules in space, is almost two orders of magnitude larger at 63K than previously measured at ~200K. We also observe formation of the methoxy radical product that was recently detected in space. These results are interpreted through the formation of a hydrogen-bonded complex that is sufficiently long-lived to undergo quantum mechanical tunnelling to form products. We postulate that this tunnelling mechanism for the oxidation of organic molecules by OH is widespread in low temperature interstellar environments.

The importance of neutral – neutral reactions has been highlighted in low temperature environments such as the interstellar medium (ISM) and in dense molecular clouds of star forming regions [1]. However, the chemical databases or networks used to model such environments contain a relatively small number of this class of reaction [2]. Those reactions that have been studied at relevant low temperatures (< 200 K) already occur quickly at room temperature, with $k_{298K} > 10^{-11}$ molecule^{-1} cm^{3} s^{-1} [3-4], and do not possess any significant barrier to reaction. In this paper, we show that despite the presence of an energy barrier, the reaction between OH and methanol proceeds to products rapidly at very low temperatures, which we interpret via a mechanism involving the formation of a weak hydrogen bonded association adduct, and quantum mechanical tunnelling, as shown schematically in Figure 1. These two features are present in many reactions involving hydrogen atom transfer and we propose that this behaviour exhibited by the reaction of methanol with OH may be widespread under the low temperature conditions found in space.

In the field of chemical kinetics, the rate at which a reaction proceeds is governed by the potential energy surface (PES) upon which that reaction occurs. If there is an overall barrier, this acts as a bottleneck to reaction and only molecules with sufficient energy are able to surmount this barrier and proceed to products. The relationship between the rate coefficient, *k*, and temperature is often represented by the Arrhenius equation:

$$\mathrm{k(T)} = \mathrm{A}e^{-\frac{\mathrm{Ea}}{\mathrm{RT}}} \tag{1}$$

where E_a is an empirical parameter which is related to the overall barrier for reaction and A is related to the frequency of reactant collisions that have the correct geometry for reaction. The rate coefficient for the reaction between OH and methanol is relatively small at room temperature [5], increasing at higher temperature as shown in Figure 2. Therefore, the reaction of OH with methanol and other reactions with a significant barrier to products have hitherto been considered too slow to be important in low temperature environments such as the ISM, dense molecular clouds of star-forming regions, or the atmospheres of other planets. However, closer inspection of Figure 2 reveals that the Arrhenius plot is curved, with the apparent activation barrier to reaction decreasing as temperature is lowered. Deviation from Arrhenius behaviour is not uncommon and it is often explained by the reaction not proceeding via a single-step, involving a weakly bound intermediate [4], or due to the presence of quantum mechanical tunnelling (QMT) [6].

Weakly bound complexes have also been invoked to explain rate coefficients that increase as the temperature is lowered [7]. Electronic structure calculations by Xu and Lin [8] for the reaction between OH and methanol have shown the presence of a weakly-bound (~ 20 kJ mol^{-1}) hydrogen-bonded complex prior to the barrier to reaction, as shown in Figure 1. However, around room temperature and above this weakly bound complex has too short a lifetime to significantly influence the reactions kinetics. Experimental [9] and theoretical [10] studies have shown that the reaction of OH with HNO_3 proceeds through tunnelling via an association complex at low temperatures, with a modest negative temperature dependence of the rate coefficient being observed below 300K. However, at the lowest temperature studied, 240 K, the measured rate coefficient (2×10^{-13} molecule^{-1} cm^3 s^{-1}) is still three orders of magnitude lower than would be expected for a barrierless reaction. In a theoretical study, Herbst [11] showed that tunnelling in the C_2H + H_2 reaction leads to an observed negative temperature dependence in the rate coefficient, but in the limit of 0 K the rate coefficient for this reaction was still predicted to be many orders of magnitude lower than would be expected for a barrierless process. We postulate that a mechanism involving a weakly bound complex may lead to rate coefficients at low temperature which are similar in magnitude to those expected for an entirely barrierless reaction. Such a mechanism could then play an important role in cold temperature environments such as in space. In this work we show experimentally that the rate coefficient for the reaction of OH with methanol increases dramatically as the temperature is lowered to 63 K. We also use the PES of Xu and Lin [8] and statistical rate theory calculations using a master equation approach to show that the formation of the OH-methanol complex and QMT can explain these findings.

Results

Figure 3 shows an example of the decay of OH radicals as they are removed by reaction with methanol at 82 K. Kinetic analysis (see Methods and Supplementary Information Figures S4 and S5) yields the removal rate coefficient, k', and the rate coefficient for the reaction of OH and methanol, k_1, the latter obtained from the dependence of k' on the methanol concentration. Figure 2 compares values of k_1 measured here at 63 K and 82 K with previous results at higher temperatures [5,12-13], demonstrating a significant enhancement in k_1 at lower temperatures, with $k_{1,T=63\text{K}} / k_{1,T=210\text{ K}} = 72$. Figure 4 shows that k_1 is essentially independent of the density of N_2 used.

The reaction of OH with methanol proceeds by abstraction of a hydrogen atom at either the methyl or the hydroxyl site, with activation barriers of 4.2 and 15.0 kJ mol^{-1}, respectively [8]:

$$OH + CH_3OH \rightarrow CH_2OH + H_2O \qquad \text{(R1a)}$$

$$OH + CH_3OH \rightarrow CH_3O + H_2O \qquad \text{(R1b)}$$

However, this reaction is not a single step. A schematic of the PES for the OH + CH_3OH reaction calculated by Xu and Lin [8] is shown in Figure 1, where it can be seen that the reaction consists of three elementary reactions:

$$OH + CH_3OH \xrightarrow{k_{1,1}} C \qquad \text{(R1,1)}$$

$$C \xrightarrow{k_{1,-1}} OH + CH_3OH \qquad \text{(R1,-1)}$$

$$C \xrightarrow{k_{1,-2}} \text{products (either R1a or R1b)} \qquad \text{(R1,2)}$$

The increase in the overall rate coefficient, k_1, at low temperature can be understood by examining how the relative contributions from these three elementary reactions change with temperature. At high temperatures the complex (C) will be formed with a significant amount of internal energy and will rapidly re-dissociate back to reactants. The reaction then appears to be a single step process over a barrier to products with k_1 displaying a normal Arrhenius behaviour, as observed at higher temperatures (Figure 2). However, as the temperature decreases C will be formed with less internal energy on average and as such its lifetime with respect to re-dissociation will increase. Therefore at very low temperatures, the rate coefficient k_1 will then be determined not by the barrier associated with process R1,2, but instead by the barrierless association R1,1, i.e. the reaction is complete once the complex is formed. The temperature at which this transition occurs is controlled by the binding energy of the complex and the rate of tunnelling through the abstraction barrier. The OH-methanol complex binding energy is ~ 20 kJ mol^{-1}, and at room temperature the kinetics are close to the high temperature regime and the rate coefficient is relatively small with $k_1 = k_{1a} + k_{1b} = 9 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} [5]. However, at the very low temperatures of the present study the complex is relatively long-lived, and thus the measured rate coefficients are closer to the collision encounter limit.

There are two possible fates for the complex at low temperatures when dissociation to reactants is very slow. Either C is stabilised through unreactive collisions with the buffer gas (N_2 in these experiments), which is not particularly interesting as this does not lead to chemical products. Alternatively the OH moiety bound in C may abstract a hydrogen atom to form products, which is chemically of greater interest. Abstraction via channels R1a and R1b over the barriers shown in Figure 1 would appear to be ruled out as there is insufficient energy. However, in the case of abstraction of light hydrogen atoms there is a significant probability of going through the barrier rather than over it via quantum mechanical tunnelling (QMT) [6]. In a single-step process, QMT normally manifests itself via non-Arrhenius behaviour being displayed at low temperatures, though still with a positive activation energy and the rate coefficient decreasing at lower temperatures. However, for the present system, QMT is not occurring in a single-step reaction from reactants to products, rather from the hydrogen-bonded complex C, which has a lifetime that is rapidly increasing as the temperature is lowered.

If the complex C were just being collisionally stabilised under our experimental conditions, the rate coefficient k_1 would be expected to be strongly dependent on the total gas number density. However, as shown in Figure 4, k_1 is almost independent of the total gas density, providing strong evidence for the proposed QMT mechanism. Tunnelling corrections to rate coefficients calculated by classical transition state theory (transmission coefficients) are now calculated routinely [14-15], and Figure 2 shows the overall rate coefficient k_1 calculated by a chemical master equation incorporating QMT using a parabolic Eckhart type barrier (see Methods and Supplementary Information). Although there are more detailed approaches to calculating transmission coefficients [16], the approach adopted here is to simply demonstrate that the weakly-bound complex/QMT mechanism is capable of showing a marked increase in the rate coefficients at lower temperatures, as seen in the experimental data in Figure 2.

To emphasize further the crucial role of tunnelling in this reaction, Figure 5 shows the calculated individual rate coefficients, $k_{1,-1}$ and $k_{1,2}$ as a function of energy, together with the initial Boltzmann distribution of energies within the complex, C, formed in the OH reaction with methanol at both 300 K and 70 K. It is important to note the crossover of the rate coefficients $k_{1,-1}$ and $k_{1,2}$ at ~1750 cm^{-1}, below which tunnelling becomes more favourable than re-dissociation of the complex. At 300 K, the Boltzmann energy distribution has a negligible population of molecules below the $k_{1,-1}$ and $k_{1,2}$ crossing point, however, at 70 K, midway between the two experimental temperatures of this study, the Boltzmann energy distribution has a significant population below this crossing point. In Figure 5, the shaded area represents the fraction of the 70 K Boltzmann distribution for which $k_{1,2} > k_{1,-1}$. It is this increase in the population of the complex with energies below the $k_{1,2}$ and $k_{1,-1}$ crossing point as the temperature is lowered that brings about the dramatic increase in the overall rate coefficient, k_1.

The probability of tunnelling is determined in part by the width of the energy barrier [6, 17]. The imaginary vibrational frequency of a transition state corresponds to motion along the reaction coordinate across the energy barrier, and to a first approximation the larger the imaginary frequency of a transition-state the narrower the barrier. Xu and Lin [8] calculated that the higher energy barrier (TS-H in Figure 1) has a substantially larger imaginary frequency of 2958 cm^{-1} compared to 1420 cm^{-1} for the lower energy barrier (TS-M). At 298 K the master equation predicts (see Supplementary Information Figure S7) that the branching ratio for the channel forming CH_3O is 0.36, which is consistent with experimental measurements which show CH_2OH is the dominant product [18]. However, at low temperatures the calculations predict that despite the larger barrier, more tunnelling occurs through TS-H giving a CH_3O branching of 0.99 at 70 K, and that CH_3O formation becomes the dominant product channel below ~250 K.

In order to provide further experimental evidence for product formation via QMT under the larger barrier, and to confirm the predictions from the master equation calculations, we undertook a search for the methoxy radical (CH_3O) product of this reaction using laser-induced fluorescence (LIF) spectroscopy, and were able to observe its formation at a rate that is consistent with the measured loss of OH radicals. Figure 3 shows the time evolution of CH_3O formed in the reaction of OH with CH_3OH at 82 K, for a fixed concentration of methanol, [CH_3OH]. As $k' = k_1$ [CH_3OH] (see methods), by varying [CH_3OH] (see insert Figure 3) the bimolecular rate coefficient for the formation of CH_3O was determined to be $(3.6\pm1.4)\times10^{-11}$ $\text{molecule}^{-1}\ \text{cm}^3\ \text{s}^{-1}$, which agreed within error with the rate coefficient for OH loss in the presence of methanol ($(3.4\pm0.5)\times10^{-11}$ $\text{molecule}^{-1}\ \text{cm}^3\ \text{s}^{-1}$) under the same conditions. These results provide strong evidence that CH_3O is being formed from the reaction of OH with methanol at very low temperatures.

In order to provide further evidence for a tunnelling mechanism, deuterated experiments were attempted (for example with CD_3OD), but these were not successful owing to the hydroxyl deuterium atom undergoing rapid exchange with hydrogen atoms from polar groups on the walls of the tubing or cylinders. Infrared spectra confirmed that the majority of the hydroxyl group deuterium atom was exchanged, creating CD_3OH, before the gases reached the Laval nozzle and reaction region.

Discussion

Both the OH radical and methanol have been observed in dense cloud environments of circumstellar envelopes. The OH radical has been observed to exhibit a fractional abundance of

~1×10^{-7} with respect to H_2 [19,20] and fractional abundances of methanol of between 1×10^{-9} to 1×10^{-7} [21] have been observed in environments varying from cold, dark clouds to protostars, being enhanced in star-forming regions. Although the temperatures in some star forming environments are close to 80 K [22], for other stellar and interstellar environments the temperatures are considerably lower, and the gas density is extremely low. In order to explore the importance of the reaction of OH with methanol under these conditions, the transition state theory calculations were extended to lower temperatures with a total gas density of 10^3 molecule cm^{-3}. By 20 K the calculated value of k_1 is predicted to be 3×10^{-10} molecule^{-1} cm^3 s^{-1} and this suggests that at temperatures relevant to the interstellar medium, almost every collision between methanol and OH would result in a successful reaction to form CH_3O (see Supplementary Information Figure S8). Currently this reaction is not included in astrochemical networks and given the high abundances of both methanol and OH in star-forming regions, these results indicate that the reaction of OH with methanol may provide a significant loss for methanol at low temperatures.

Recently the methoxy radical, CH_3O, has been observed in space in a cold and dense core (B1-b) using radio astronomy [23], with an abundance of ~ 10^{-11}. However, laboratory experiments performed in the same study with ice mantle proxies indicated that the CH_3O isomer released to the gas phase is CH_2OH rather than the methoxy radical, suggesting that CH_3O formed in the mantle preferably isomerises to CH_2OH or leads to methanol formation. Hence in order to explain the astronomical observation of CH_3O in B1-b [23], a gas phase source was required, with one candidate being the fast reaction of OH with methanol as we have observed.

These features are not unique to the reaction of OH with methanol, with many other hydrogen atom transfer reactions proceeding over energy barriers likely to exhibit similarly large rate coefficients at low temperature. For example, the reaction between OH and NH_3 (another abundant molecule in space [24]) has a weakly bound pre-reactive complex (6.6 kJ mol^{-1}) and a barrier to reaction (12.9 kJ mol^{-1}), and the rate coefficient is small at room temperature, displaying a normal Arrhenius dependence at higher temperatures [25]. Calculations using MESMER show that, as in the methanol case, the reaction of OH with NH_3 increases rapidly at very low temperatures due to the weakly bound complex/QMT mechanism, and consistent with preliminary measurements [26].

In conclusion, this study has shown that for the reaction between OH and methanol the rate coefficient displays a large negative dependence on temperature below 200 K, with an increase of about two orders of magnitude at ~70 K. Furthermore, we observe formation of the of CH_3O product through a significant energy barrier, consistent with statistical rate theory calculations in which inclusion of a quantum mechanical tunnelling mechanism is required to reproduce the observed temperature dependence. Tunnelling control of a chemical reaction through a pathway with a higher barrier was recently reported for isomerisation of a carbene intermediate [27]. These results further highlight the role that a pre-reaction hydrogen bonded OH complex plays in low temperature kinetics, in this case the adduct is sufficiently long lived to facilitate tunnelling, the majority proceeding via the higher activation barrier to form CH_3O. In previous studies, for example of the reaction between OH with acetone, we had also observed a dramatic increase in the rate coefficient at very low temperatures [28], although a significant pressure dependence of the rate coefficient suggested collisional stabilisation of the complex without tunnelling to products [26]. Hydrogen bonded complexes occur on the PES of many other reactions involving neutral species, and we postulate that hydrogen transfer reactions occurring over a significant energy barrier, and which were previously assumed to be negligibly slow in very low temperature environments, could exhibit a similar negative temperature dependence to the one observed here.

Methods

We have used a pulsed Laval nozzle apparatus to study the kinetics and product formation for this reaction at 63 and 82 K. This method is described in detail elsewhere [29] (see Supplementary Information and Figure S1) and involves a pulsed, isentropic expansion of gas through a specially shaped convergent-divergent nozzle producing a collimated flow of gas at thermal equilibrium. OH radicals are generated along the entire flow of gas using excimer laser-flash photolysis of *t*-butyl hydroperoxide (*t*-BuOOH) at 248 nm, and are monitored using time-resolved laser-induced fluorescence (LIF) spectroscopy using the $A^2\Sigma^+$-$X^2\Pi_i$ (1,0) $Q_1(1.5)$ transition at ~282 nm. By varying the time delay between the photolysis and the LIF laser, the temporal evolution of OH is recorded. All experiments were performed under pseudo first order conditions, with $[CH_3OH] >> [OH]$, so that $[CH_3OH]$ can be assumed to be constant over the course of the reaction, and the OH time profile is given by:

$$[\mathrm{OH}] = [\mathrm{OH}]_0 \, \mathbf{e}^{-(k'+k_d)t} \qquad (2)$$

where $[OH]_0$ is the concentration of OH at time zero, $k' = k_1$ $[CH_3OH]$, k_d is the rate coefficient for loss of OH by reaction with the *t*-BuOOH precursor and by diffusion. A plot of $(k' + k_d)$ versus the concentration of methanol yields the bimolecular rate coefficient for the reaction (k_1) from the gradient and k_d from the intercept. For experiments in which the CH_3O was detected as a product of the reaction of OH with methanol, OH radicals were produced using the reaction of $O(^1D)$ with H_2 and the resulting CH_3O radicals were probed using LIF using the $\tilde{A}^2A_1$-$\tilde{X}^2E$ band close to 297 nm. The time resolved growth in the LIF signal due to CH_3O formation was then fit to a function of the form:

$$[\mathrm{CH_3O}] = \frac{k'[\mathrm{OH}]_0}{k_{dm} - k' - k_d} \left(e^{-(k'+k_d)\times t} - e^{-k_{dm}\times t}\right) \qquad (3)$$

where k' and k_d are the same constants as described in equation 1 and k_{dm} is the first order loss of CH_3O. As $k' = k_1$ $[CH_3OH]$, by varying $[CH_3OH]$ the bimolecular rate coefficient for the formation of CH_3O was determined.

Statistical rate theory calculations were performed for the potential energy surface calculated by Xu and Lin [8] using the master equation software MESMER (Master Equation Solver for Multi Energy-well Reactions) [30]. Microcanonical rate coefficients for the barrierless association of OH and methanol to form the complex C were calculated using an inverse Laplace transform method [31] and microcanonical rate coefficients for the hydrogen abstraction processes occurring via either TS-H or TS-M (see Figure 1) were calculated using Rice, Ramsperger, Kassel and Marcus (RRKM) theory. In order to incorporate quantum mechanical tunnelling, transmission coefficients for tunnelling were calculated using a parabolic Eckhart type barrier. In this method the shape of a given energy barrier is approximated using the imaginary frequency of the appropriate transition state as described by Miller [32]. Further details of the experimental and theoretical methods used are given in the Supplementary Information.

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Author contributions

R.J.S., M.A.B., A.G. and D.E.H. conceived and designed the experiments and analysed the data. R.J.S. and M.A.B. performed the experiments. R.J.S., M.A.B. and D.E.H. co-wrote the paper.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to D.E.H.

Competing financial interests

The authors declare no competing financial interests.

Figures and figure captions

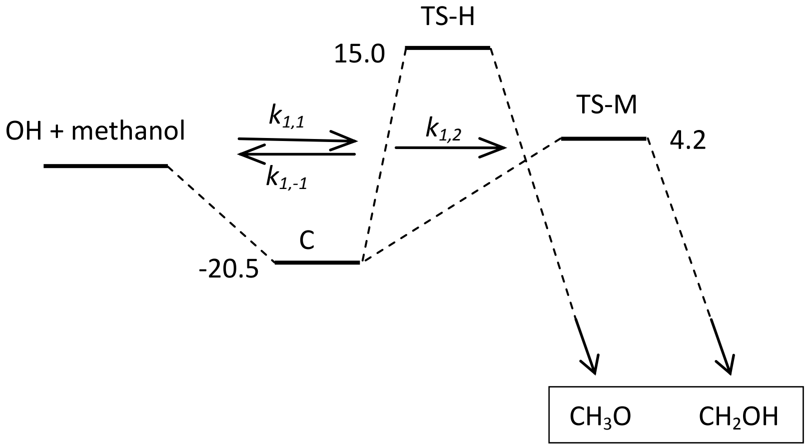

Figure 1. Schematic potential energy surface for the reaction between OH and methanol based on the calculations of Xu and Lin [8] with all energies given in kJ mol^{-1} relative to the reagents. C refers to the pre-reaction hydrogen bonded complex formed between OH and methanol molecules, and TS-H and TS-M represent transition states located at the barriers to hydroxyl and methyl-hydrogen atom abstraction, respectively. The macroscopic rate coefficients $k_{1,1}$ and $k_{1,-1}$ correspond to the formation and re-dissociation of the complex and $k_{1,2}$ corresponds to hydrogen abstraction via either of the two transition states.

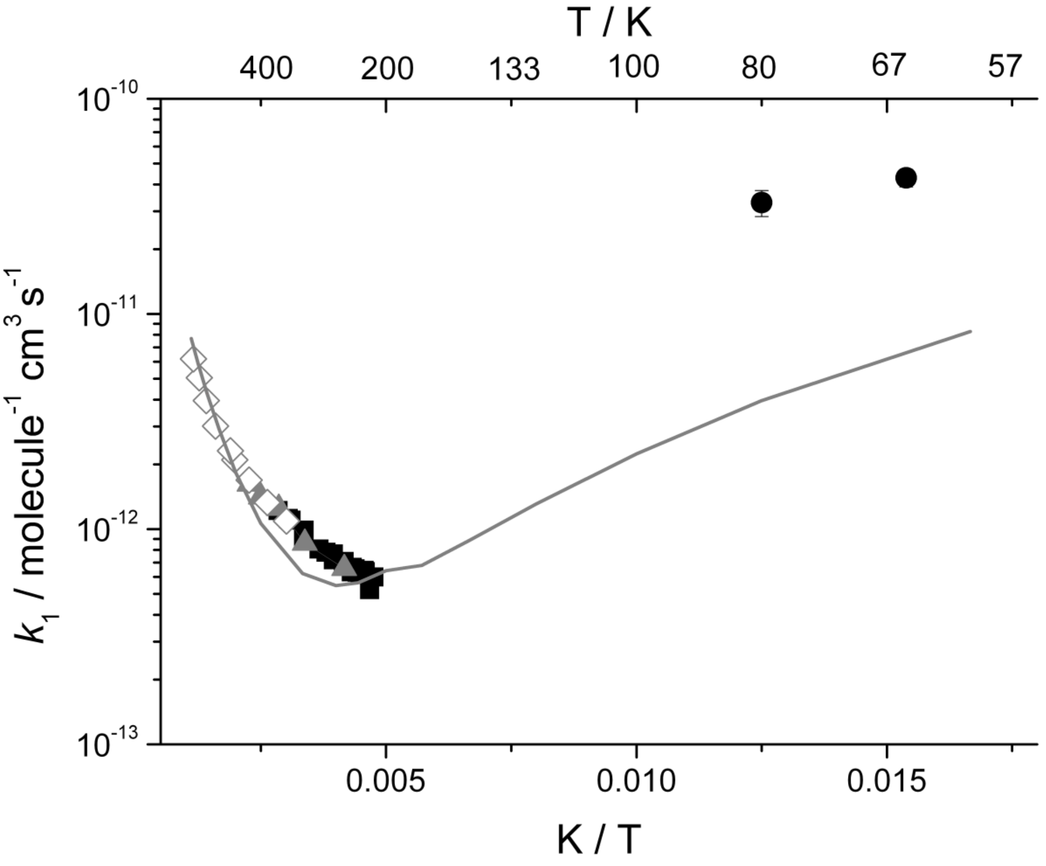

Figure 2. Temperature dependence of the rate coefficient k_1 for the reaction of OH radicals with methanol plotted in Arrhenius form together with a theoretical calculation. Data above 200 K are taken from a representative sample of literature data. Black squares Dillon *et al.* (2005) [5]; Open diamonds Hess *et al* (1989) [12]; Grey triangles Wallington and Kurylo (1987) [13]. The black filled circles are experimental data from the current study with 2σ error bars and the data point at 82 K is an average of the three rate coefficients measured at different [N_2]. The solid line is the calculation using the master equation incorporating quantum mechanical tunnelling.

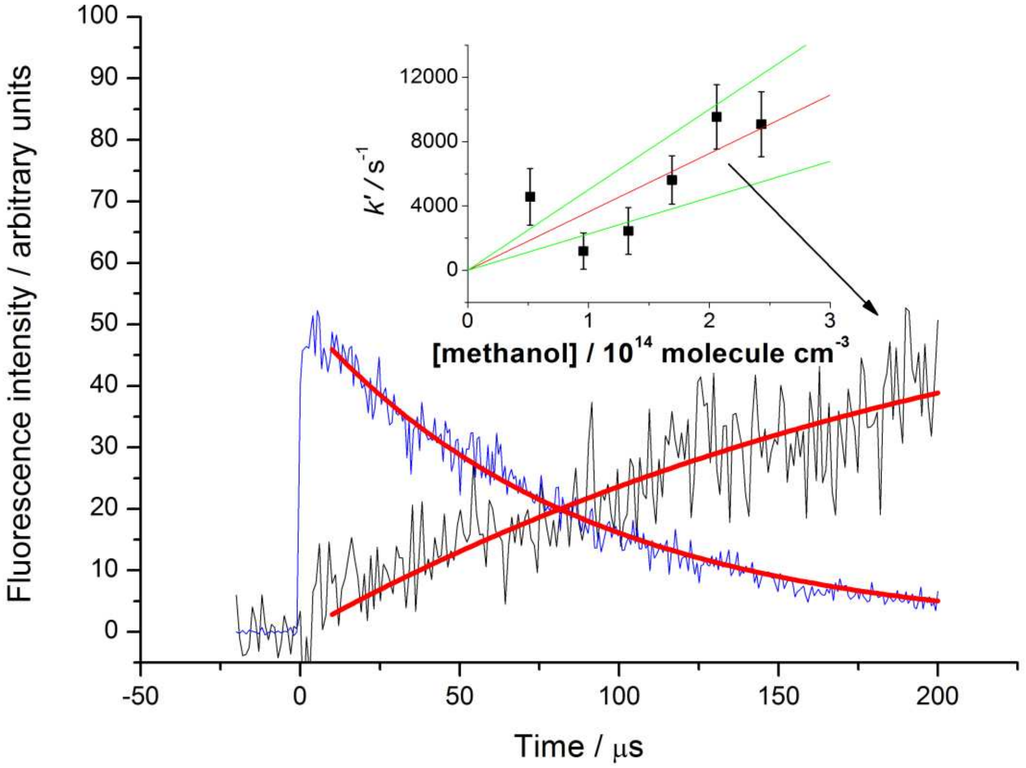

Figure 3. Removal of hydroxyl (OH) radicals and production of methoxy (CH_3O) radicals in the reaction of OH with methanol at 82 K. Main figure: The temporal evolution of the decay of OH radicals (blue points) and the production of CH_3O radicals (black points) at 82 ± 4 K, for a total gas density of 5×10^{16} molecule cm^{-3} and $[CH_3OH] = 2.06\times10^{14}$ molecule cm^{-3}. The red solid lines are fits of the function A exp($-k't$) (decay) and Equation 1 (growth) to the data, which yields pseudo-first-order rate coefficients of $k' = 8600 \pm 280$ s^{-1} (decay of OH) and 8870 ± 2800 s^{-1} (formation of CH_3O), respectively. The black points for CH_3O are scaled by a factor of 20 to aid comparison. Inset: Bimolecular plot showing the increase in the pseudo-first-order rate coefficients of k' for the formation of methoxy radical as a function of $[CH_3OH]$, which yields the rate coefficient $(3.6\pm1.4)\times10^{-11}$ $molecule^{-1}$ cm^3 s^{-1}.

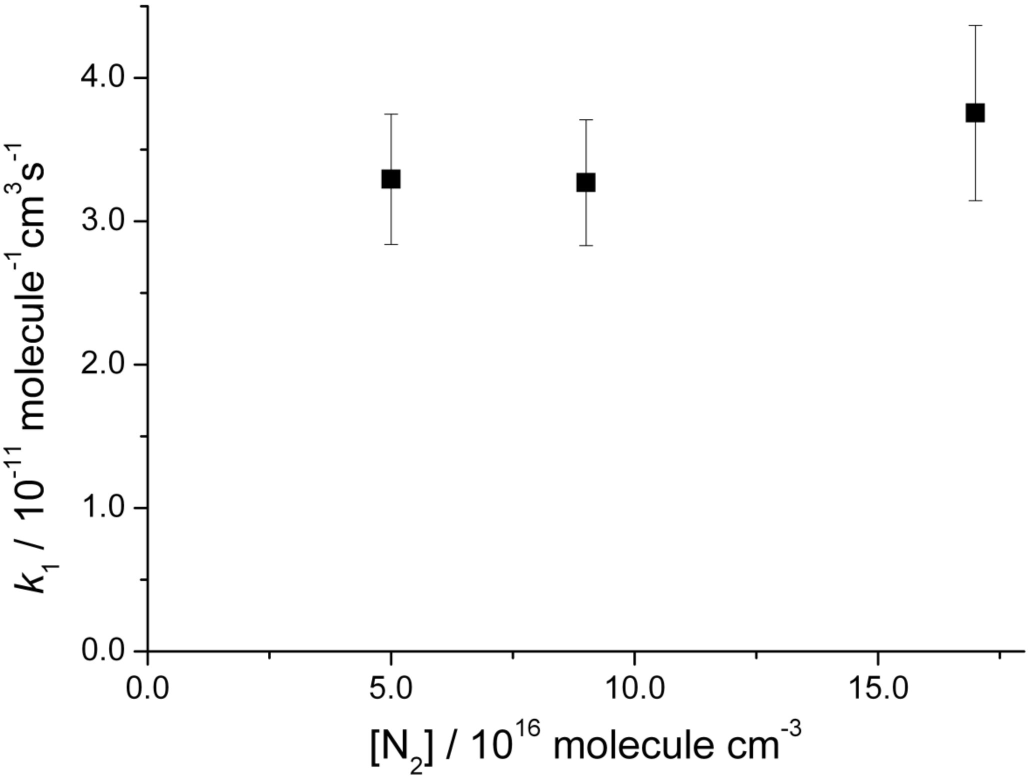

Figure 4. Variation of the rate coefficient for the reaction of OH with methanol as a function of total gas density at 82 ± 4 K. The uncertainty for each determination of k_1 represents the 2σ error from a linear-least squares fit to the variation of the pseudo-first-order rate coefficient k' for the removal of OH as a function of methanol concentration (for an example see Figure S5). The bath gas used is nitrogen.

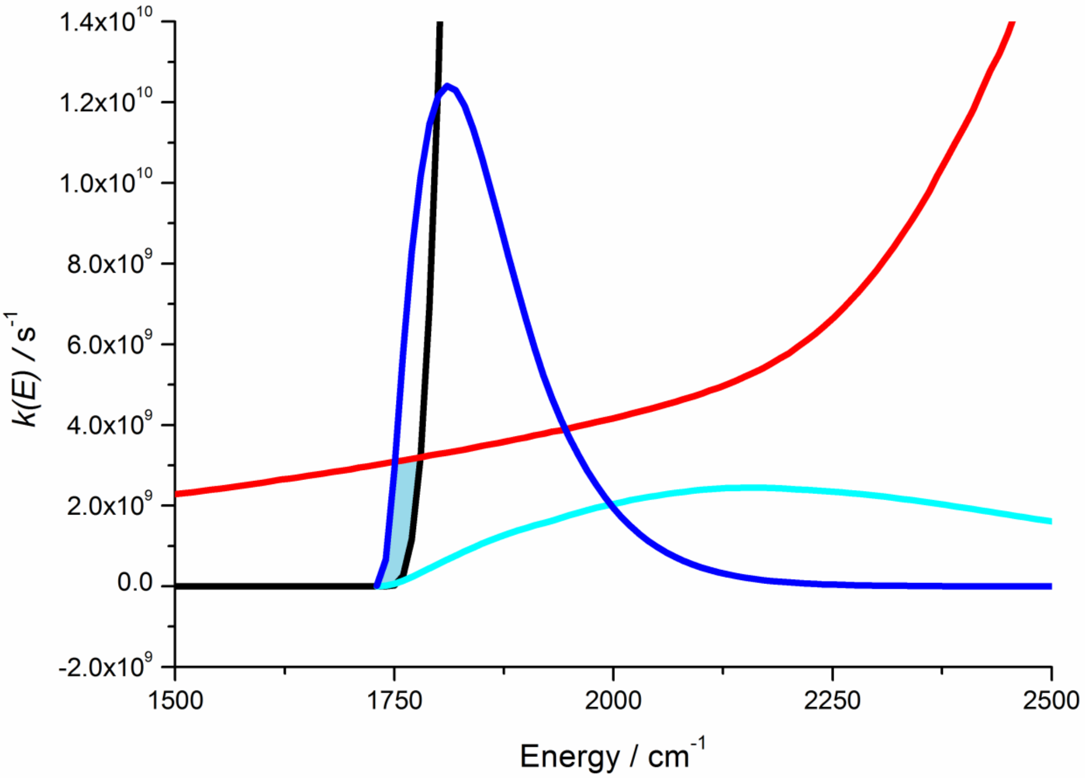

Figure 5. Rate coefficients for the dissociation back to reactants (black line) and the product forming channel (red line) as a function of energy within the initially formed OH-methanol complex. The microcanonical rate coefficients $k_{1,-1}$ (black) and $k_{1,2}$ (red) calculated as a function of energy within the OH-methanol complex using the chemical master equation. The initial relative Boltzmann distribution of energies within the complex at 300 K (cyan line) and 70 K (blue line) (values not shown on axis for clarity) are also shown. The shaded portion represents the fraction of the 70 K Boltzmann population that have energies for which $k_{1,2} > k_{1,-1}$. Only the 70 K Boltzmann distribution has a significant population for which for which $k_{1,2} > k_{1,-1}$. The energy scale is shown relative to the bottom of the hydrogen bonded complex C (see Figure 1), which is bound by 1715 cm^{-1} (20.5 kJ mol^{-1}).