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Rapid acceleration of hydrogen atom abstraction reactions of OH at very low temperatures through weakly-bound complexes and tunnelling

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CONSPECTUS

A generally accepted principle of chemical kinetics is that a reaction will be very slow at low temperatures if there is an activation barrier on the potential energy surface to form products. However, this Account shows that the reverse is true for gas-phase hydrogen abstraction reactions of the hydroxyl radical, OH, with organic molecules with which it can form a weakly-bound (5-30 kJ mol^{-1}) hydrogen-bonded complex. For hydrogen atom abstraction reactions of OH with volatile organic compounds (VOCs) containing alcohol, ether, carbonyl and ester functional groups, the reaction accelerates rapidly at very low temperatures, with rate coefficients, *k*, that can be up to a 1000 times faster than at room temperature, despite the barrier to products. The OH radical is a crucial intermediate in Earth's atmosphere, combustion processes and the chemistry of the interstellar medium, where temperatures can reach as low as 10 K, and so this behaviour has very important implications for gas-phase chemistry in space. The key point is that at low temperatures the lifetime of the OH-VOC complex against re-dissociation back to reactants becomes much longer, and hence the probability of quantum mechanical tunnelling under the reaction barrier to form products becomes much higher. These observations were made possible by using Laval nozzles to generate uniform supersonic flows at extremely low temperatures, so that condensation of the reagents at reactor walls is avoided. In this Account the use of laser flash-photolysis combined with laser-induced fluorescence spectroscopy within Laval flows is described to study the unusual kinetics of this type of reactions at temperatures down to 21 K, and demonstrate the rapid upturn in the rate coefficient. For the reaction of OH with CH_3OH, further evidence for the pre-complex and tunnelling mechanism comes from observation of the CH_3O reaction product at very low temperatures, despite it being formed over the higher barrier to reaction. The experimental observations are supported by theoretical calculations using the MESMER master equation package to calculate $k(T)$ and product yields as a function of temperature, and which make use of potential energy surfaces determined using ab initio methods. The CH_3O product is formed over a narrower barrier with a larger imaginary frequency, and is calculated to be the sole product at very low temperatures. The kinetics of the OH reaction with CH_3OH were measured to be independent of pressure, consistent with a tunnelling mechanism rather than any collisional stabilization of the pre-reactive complex. In this Account we collate available kinetic data and show that this newly discovered mechanism for H-atom transfer reactions appears to be generally applicable for reactions of OH with organic molecules containing oxygenated functional groups, which have been observed in space by radio-astronomy. Rather

than being ignored for a range of interstellar environments, these OH reactions are now being included in chemical networks in space, and have been shown to significantly influence the abundance of OH, the organic molecules themselves and reaction products, and provide novel routes to forming even more complex functional groups, for example precursors to pre-biotic molecules.

1. INTRODUCTION

The transfer of a hydrogen atom is a critical chemical step in many important applications, including, for example, processes in Earth's atmosphere and those of other planets, astrochemistry of the interstellar medium (ISM), and combustion processes. In Earth's atmosphere and during the combustion of fossil and alternate fuels (e.g. biofuels), chemical oxidation is often initiated by reaction with the hydroxyl radical, OH, referred to as Nature's detergent[1]. For saturated hydrocarbons, the rate determining step is the initial abstraction by OH of an H atom to form water vapour, usually a highly exothermic process. The abstraction reaction has an activation barrier, E_a, and therefore the rate coefficient, k, is predicted to drop to very small values at low temperatures according to the familiar Arrhenius equation:

$$k = A\ exp\ (-E_a / RT) \qquad \text{(E1)}$$

For this reason, reactions with activation barriers have usually been neglected when constructing the chemical networks used to describe the evolution of molecular species in space, where temperatures are extremely low, down to 10 K in the interstellar medium[2,3]. Around 200 molecules have now been detected in the interstellar medium or circumstellar shells, and 62 in extragalactic sources, many of which are complex organic molecules (COMs), defined as having 6 atoms or more (see https://www.astro.uni-koeln.de/cdms/molecules). A key question is how these COMs are formed and destroyed, and how their chemistry relates with the formation of pre-biotic precursors such as formamide ($HC(O)NH_2$), which is widely observed in space.[4] The detection of pre-biotic molecules themselves in molecular clouds, such as the simplest amino acid glycine ($NH_2CH_2C(O)OH$), is controversial. Gases constitute ~ 99% of the mass of the interstellar medium, with the remaining ~1% being cosmic dust. However, despite dominating the mass, gas phase reactions involving H-atom transfers are often neglected as routes for COM formation or destruction, in particular reactions between neutral species, as they were assumed to be too slow owing to the activation barrier. Instead, reactions on dust grains (or on icy mantles surrounding the core) where barriers are lower have been proposed to account for the formation of the majority of COMs in the Universe.[5]

These assumptions were challenged recently by the realization that the rate of some neutral-neutral gas-phase reactions with barriers can accelerate rapidly at the very low temperatures found in space[6-13]. In this Account this behaviour is reviewed for a number of reactions of OH with COMs containing a variety of functional groups, and which are characterized by the formation of a weakly-bound hydrogen-bonded complex in the entrance channel.

2. NON-ARRHENIUS KINETIC BEHAVIOUR WITH TEMPERATURE

The functional dependence of k with temperature, T, can take a variety of forms depending on the type of potential energy surface describing the reaction[14]. Many reactions have a simple activation barrier and follow Arrhenius behaviour given by Equation (1) over a range of temperatures, with a positive temperature dependence and a linear variation of ln *k* plotted versus $1/T$, which yields E_a as the gradient. Mild upward curvature is sometimes observed at low temperatures owing to quantum mechanical tunnelling for transfer of light atoms, such as hydrogen. The approach of two radicals on a barrierless surface forms an intermediate complex, which either decomposes to products without a barrier, or forms a stable association product following collisional stabilization. Highly non-Arrhenius behaviour is observed, with *k* increasing at lower temperatures corresponding to a negative E_a. This Account considers another type of reaction mechanism, the barrierless formation of a weakly bound and transitory complex between the two reagents in the entrance channel, followed by a second step with an activation barrier corresponding to the breaking and re-forming of chemical bonds to form the reaction products. If the barrier is below the reactant asymptotic energy (a "submerged barrier"), then there is no overall activation barrier to reaction. Alternatively (and the topic of this Account) the barrier is above the reactant asymptotic energy, as shown in Figure 1, resulting in a highly complex variation of *k* with *T*. For reactions of OH with organic compounds containing oxygenated functional groups, the complexes are bound via hydrogen bonding. At higher *T*, a significant fraction of the collisions are sufficiently energetic to surmount the barrier directly, and so normal Arrhenius behaviour is observed. However, at lower temperatures the lifetime of the hydrogen-bonded complex increases, as it is formed with less internal energy, and so the rate of its decomposition back to reactants decreases, and quantum mechanical tunnelling through the barrier to reaction is able to compete to form products, and so the rate coefficient begins to increase once again. The role of hydrogen-bonded intermediates in controlling the kinetics of bimolecular reactions of OH radicals was reviewed by Smith and Ravishankara in 2002.[15] For example, for the reaction:

$$\mathrm{OH + HNO_3 \rightarrow NO_3 + H_2O} \qquad \text{(R1)}$$

which is important in Earth's stratosphere, the rate coefficient over the range 375 – 225 K displays a distinct minimum before increasing at low temperature. However, the absolute change in *k* was relatively modest, only about a factor of 2, and the values of *k* at the two extremes of *T* were similar. The OH radical forms relatively stable hydrogen bonded complexes with oxygenated VOCs, for example alcohols, ethers, aldehydes, ketones and esters, with binding energies varying from ~5-30 kJ mol^{-1}.[15]. The kinetics of these species are well established above ~200 K using standard apparatus where there is little condensation at the reactor walls. For several of these reactions, for example those of OH with ketones[16] and acetals,[17] a distinct minimum in *k* indicating a change in mechanism is observed close to or even above room temperature.

3. THE PULSED LAVAL NOZZLE METHOD FOR THE STUDY OF THE KINETICS OF OH WITH OXYGENATED VOCS AT VERY LOW TEMPERATURES

Cryogenic cooling results in condensation at reactor walls for less volatile species, and a free-jet expansion, although capable of generating temperatures below 1 K, is a difficult environment in which to study kinetics, owing to very large gradients in both temperature and density. A crossed-beam apparatus capable of determining absolute reactive cross-sections with varying collision energies can be used to determine energy dependent rate coefficients *k*(*E*), and hence *k*(T) for very low *T* following appropriate averaging. However, in practice it is very difficult to generate absolute reactive cross-sections to implement this method. The use of Laval nozzles for low temperature studies of chemical kinetics, both for neutral and charged species, has been reviewed extensively[12], and the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) method is described only briefly. As shown in Figure 2, a Laval nozzle has a converging-diverging shape, and if designed correctly generates a collimated supersonic flow of known and uniform temperature and density for an extended distance from the nozzle. Although a Laval nozzle with a continuous flow of gas can reach extremely low temperatures (the current record being 6 K[12]), the volumetric flow rates and the size of the pumps are enormous. It is very difficult to entrain a sufficient amount of a reagent with a low vapour pressure (usually at ~0.1-1% of the total flow), and more recently pulsed Laval nozzles have been developed, capable of generating pulsed flows of 10-20 ms in duration down to ~ 22 K,[18] which use much less gas and employ standard sized pumps. In order to characterize the uniform flow from the Laval nozzle flow, a pitot tube is placed in the flow and the impact pressure measured with a differential pressure transducer. The impact pressure is related via the Rayleigh equation to the Mach number of the flow,[19] which is turn can be used to calculate the temperature and density of the flow for the particular bath gas used. The translational temperature obtained in this way has been shown to be in good agreement with the rotational temperature of the reagents, determined by molecular thermometry, for example by laser-induced fluorescence (LIF) spectroscopy.[19]

The standard method to determine a rate coefficient, k, for the reaction:

$$\text{OH} + \text{VOC} \xrightarrow{\text{k}} \text{products} \tag{R2}$$

within the flow from a Laval nozzle is laser-flash photolysis combined with LIF, as shown schematically in Figure 2. OH is generated from H_2O_2 or $(CH_3)_3COOH$ at 248 nm using an excimer laser, and its subsequent temporal profile is measured using LIF using a pulsed dye-laser. In the simplest case, the OH profile is given by:

$$[\text{OH}] = [\text{OH}]_0 \exp(-k_{\text{obs}}\, t) \quad \text{or} \quad \ln[\text{OH}] = \ln[\text{OH}]_0 - k_{\text{obs}}\, t \tag{E2}$$

where $k_{obs} = k$ [VOC] + k_{loss} is the pseudo-first-order rate coefficient, with k_{loss} being the rate of removal of OH via diffusion or via reaction with the precursor molecule. k_{obs} is obtained by fitting equation (E2) to the experimental data, as shown for OH+propan-2-ol in Figure 3, and k is obtained for a given temperature from the gradient of k_{obs} plotted versus [VOC], as illustrated again for OH + propan-2-ol in Figure 3. A limitation of the Laval method is the limited length of the stable flow and hence the reaction time within the uniform flow (typically a few 100 µs, dependent upon Mach number) and the limited concentration of the VOC (held in excess) which can be added. The limit is to maintain the stability of the flow, whose properties are defined by the bath gas used (usually He, Ar or N_2), and also to avoid the possible formation of dimer species[20], meaning that typically only rate coefficients > ~10^{-13} cm^3 $molecule^{-1}s^{-1}$ can be measured.

4. REACTIONS OF OH WITH OXYGENATED VOCS AT VERY LOW TEMPERATURES

Figure 4 collates the temperature variation of $k(T)$ and also the ratio $k(T)/k_{300K}$ for a number of reactions of OH with oxygenated VOCs, for which there is a distinct minimum in $k(T)$.

4.1. The reaction of OH with methanol

Astronomical observations of both the OH radical and methanol have been made in dense molecular clouds of circumstellar envelopes.[2,8] 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]

$$OH + CH_3OH \xrightarrow{k_{3a}} CH_2OH + H_2O \qquad (R3a)$$

$$OH + CH_3OH \xrightarrow{k_{3b}} CH_3O + H_2O \qquad (R3b)$$

A schematic of the potential energy surface is shown in Figure 5, with the reaction proceeding via the formation of a weakly-bound hydrogen-bonded complex (k_a), which can either re-dissociate back to reactants (k_{-a}), or form products via channels (R3a) or (R3b) (k_r). At higher temperatures, the complex dissociates very rapidly (k_{-a} is very large) and plays no role in the kinetics of the reaction and the reaction proceeds via a single step displaying normal Arrhenius kinetics, with the major product being CH_2OH after surmounting the lower barrier to reaction via TS-M (Figure 5). The rate coefficient, $k_3 = k_{3a} + k_{3b}$, displays a positive temperature dependence above 200 K, but since 2013 two groups[7,8,11] using pulsed Laval nozzles have shown that k_3 displays a dramatic upturn at lower temperatures, as shown in Figure 6, with $\frac{k_{3,22\,K}}{k_{3,200\,K}} \sim 100$.

Practitioners of the Laval nozzle technique are always very careful to check that dimer species do not play a role,[11,20] by ensuring that second order plots of the type shown in Figure 3 are linear. At higher concentrations of the VOC, curvature is sometimes observed, but these concentrations are never used in the kinetic analysis to obtain k. For OH+methanol, an independent experimental method using a cold flow-tube that did not rely on the supersonic expansion of a gas through a Laval nozzle confirmed the rapid upturn in the rate coefficient below 200 K,[7] and data points from this method between 123 and 202 K are included in Figure 6 . The agreement of two independent methods provides confidence in the observed trend in $k_3(T)$.

A possible fate of the weakly bound OH-methanol complex is collisional stabilisation into the well (binding energy 20.5 kJ mol^{-1} or 1715 cm^{-1}), as shown schematically in Figure 1, so that re-dissociation to the reagents, one of which is the monitored OH, is not possible. Stabilisation would therefore result in a larger rate coefficient which would then be expected to be pressure dependent. However, k_3 was found to be independent of the total density used in the Laval flow[8], providing evidence that the reaction is purely bimolecular and the enhanced rate of reaction at low temperature for OH+methanol is due to quantum mechanical tunnelling through the barrier to reaction to form products (k_r in Figure 5). Another possibility is that the reaction is termolecular (involving a third body) and k_3 is at its high pressure limit, k_∞. In order to rule this out, an estimate of k_∞ was obtained experimentally at ~ 88 K by monitoring the loss of OH(v"=1) using the so called proxy method.[21] An assumption is made that following formation of the OH(v"=1)-CH_3OH complex, there is rapid redistribution of vibrational energy amongst the modes of the complex, and only OH(v"=0) will emerge when the complex re-dissociates. Hence by monitoring OH(v"=1), the capture rate coefficient for complex formation, $k_a = k_\infty$ is estimated. The value of k for OH(v"=1)+CH_3OH was found to be $(1.50\pm0.21)\times10^{-10}$ cm^3 $molecule^{-1}s^{-1}$,[22] a factor of 4 higher than the pressure independent value obtained for OH(v"=0) at 88 K.

Although the absolute yield was not measured, the CH_3O product, formed by tunnelling through the *higher* barrier to reaction via TS-H (Figure 5), was observed using LIF, providing strong support for the tunnelling mechanism, and its rate of formation was consistent with the rate coefficient obtained from the measured decay of OH.[8] The formation of the CH_3O product via the higher barrier seems counterintuitive, but one must remember that the probability of tunnelling is controlled in part by the frequency of the motion associated with tunnelling, which is an imaginary value owing the potential going through a maximum at the barrier. The barrier forming CH_3O product via TS-H is narrower, with an imaginary frequency of $\bar{\nu}$ =2958 cm^{-1}, compared with that forming CH_2OH via TS-M ($\bar{\nu}$ =1420 cm^{-1}). Similar behaviour has been observed for other reactions in the solid state.[23,24]

There have been several theoretical studies of the OH+methanol reaction[25,26], most focusing on behaviour above 200 K, but also at lower T's relevant to the Laval nozzle experiments.[25] The open source master equation solver MESMER (Master Equation Solver for Multi Energy well Reactions)[27] was used to calculate individual rate coefficients, $k(E)$, as a function of energy within the complex both for re-dissociation to reactants and tunnelling to form products. MESMER uses a potential energy surface calculated from quantum theory, considers both reactive and energy transfer processes and can incorporate tunnelling (using either an asymmetric Eckhart barrier or a semi-classical Wentzel–Kramers–Brillouin (WKB) method to approximate the barrier potential) in order to calculate phenomenological rate coefficients for comparison with experiment.[27] For energies in the complex below ~ 1750 cm^{-1}, the tunnelling reaction occurs on a timescale short compared to the dissociation. At 300 K there is a negligible population of molecules below this energy, but this population increases extremely rapidly at very low temperatures, leading to the dramatic increase in k_3 at low temperatures shown in Figure 6.[8] MESMER is able to reproduce the general shape of the upturn of $k_3(T)$ at low temperatures, but was not able to give quantitative agreement. A recent theoretical study also probed the shape of k_3 at low temperatures, and found a significant effect of the anharmonicity of high-frequency modes of transition states, and showed that tunnelling led to an unusual negative temperature dependence below 100 K.[25] The rate of tunnelling is expected to decrease dramatically for deuterated methanol, but unfortunately rapid exchange of D with H via the walls of the gas-lines led to the formation of CD_3-OH, and any so effect could not be studied experimentally.[8]

The spectroscopy and dynamics of weakly-bound complexes between OH and other species have been extensively studied in free-jet expansions[28] and, more recently, following their stabilisation within helium nanodroplets.[29] Using a serial pick-up process, OH and methanol reagents were encapsulated within helium nanodroplets, and following formation of the complex, rapid energy exchange with the He bath stabilised the complex at the bottom of the well shown in Figure 5. The droplets were then passed through a Stark multipass cell and the infrared absorption spectrum of the complex measured, revealing a wide-amplitude bending motion which sampled the transition state geometry for the reaction of OH with methanol to form CH_3O product.[29] These spectroscopic experiments provide evidence for the existence of the hydrogen-bonded pre-reactive complexes which lead to the dramatic upturn in rate coefficients for these reactions at very low temperatures.

The very large enhancement of the reactivity between OH and methanol at low temperatures has important implications for interstellar chemistry, both as a sink for methanol, and as a source of CH_3O, which was first observed by radio-astronomy in 2012,[30] and the other product, water vapour. The rate coefficient has now been measured down to 22 K, and from parameterisations of the kinetic data with temperature[11], as well as MESMER master equation calculations exploiting ab initio potential energy surfaces, the rate coefficient can be extrapolated with confidence down to 10 K, relevant for cold, dark clouds, for example Barnard B1-b.[30] The yield of CH_3O is calculated to be unity for temperatures below 100 K calculated using MESMER and the two-transition state surface shown in Figure 5.[8] Using a gas-grain model chemical network with both gas-phase and dust-particle surface reactions (12,000 in total), the impact of the OH-methanol reaction was studied at 10, 50 and 100 K for conditions typical of a dense molecular cloud.[31] As shown in Figure 7, including this reaction led to a 100% and 25% increase in the abundance of CH_3O and H_2O, respectively, and a 10% decrease in CH_3OH, for an evolving time of $\sim 10^6$ years. In another modelling study constrained with the conditions in the cold core Barnard 1b, where methanol has a wide distribution, a previously developed gas-phase reaction network including the new kinetic data for the OH+CH_3OH reaction predicted a CH_3O/CH_3OH abundance ratio similar to astronomical observations.[11]

4.2. The reaction of OH with ethanol and propan-2-ol

For ethanol above 200 K, abstraction at the methylene (-CH_2) centre is the dominant channel[32], consistent with theoretical predictions that this has the lowest barrier. By analogy with methanol, the CH_3CH_2O product might be expected to become the main product at very low temperatures, but as no attempt was made to detect this product by LIF, this could not be confirmed. For propan-2-ol, abstraction from the CH group (central C atom containing the –OH group) is calculated to be barrierless[33], in agreement with experiment[34]. Despite the observation of ethanol in a variety of astrophysical locations[13] (propanol has not yet been observed), kinetic studies below 200 K were only recently conducted by groups using a pulsed Laval nozzle down to 21 K.[6,13] The rate coefficient increases dramatically below 200 K as shown in Figure 4, with $\frac{k_{21\,K}}{k_{300\,K}} \sim 100$. At T~20-50 K, k from both studies appears independent of total pressure. Around T=80-90 K there is perhaps a small pressure dependence,[13] although this is difficult to discern owing to the experimental uncertainties. Monitoring the loss of OH(v">0) and using the proxy method[21] suggested that the reaction is not at the high pressure limit.[6] For OH+propan-2-ol, previous measurements showed that k is independent of T between 250-750 K, whereas a single Laval nozzle study showed that $\frac{k_{88\,K}}{k_{298\,K}} \sim 10$.

4.3. Reaction of OH with di-methyl-ether (DME)

There have been extensive studies of the kinetics of the reaction:

$$OH + CH_3OCH_3 \xrightarrow{k_4} CH_3OCH_2 + H_2O \qquad (R4)$$

particularly at higher temperatures relevant to combustion.[35] DME has also been widely observed in space, for example in the Sagittarius B2 molecular cloud,[2,3] and can be generated from the reaction of CH_3 with CH_3O,[2] the low temperature product of the OH+CH_3OH reaction, followed by radiative association. As shown in Figure 4, k_4 increases by about a factor of 10 from 200 K to 63 K, and also increased with pressure.[9] Evidence for production of the product, CH_3OCH_2, via quantum mechanical tunnelling from a stabilized complex, came indirectly from experiments performed in the presence of O_2, which can recycle OH via the reaction:

$$CH_3OCH_2 + O_2 \rightarrow CH_3OCH_2O_2^* \rightarrow OH + 2\ H_2CO \qquad (R5)$$

The yield of the CH_3OCH_2 abstraction product via analysis of the reduction of k_4 in the presence of O_2 was estimated to be ≥ 50% at 93 K. Transition state theory was used to calculate k_4 over a very wide range of T, and was able to capture both the high temperature behaviour, as well as the dramatic upturn in the rate coefficients measured in the Laval nozzle for $T < 100$ K.[36]

4.4. Reactions of OH with acetone and methyl-ethyl ketone

A very dramatic increase in the rate coefficient for OH+acetone at low temperatures is observed, as shown in Figure 4, with $\frac{k_{86\,K}}{k_{295\,K}} = 334$, and unlike the other systems, a *marked* pressure dependence was observed, as also shown in Figure 8.[9] The results are indicative of collisional stabilization of the pre-reaction complex, but the intercept supports a significant zero pressure channel to products via tunnelling. Calculations were performed with the master equation package MESMER[27] using an ab initio surface for the reaction, and which included a treatment of tunnelling. MESMER was able to reproduce the trend of k(T) for 70 – 800 K, and using a modified Lindemann-Hinshelwood mechanism, the pressure dependence of k at 80 K as shown in Figure 8.[9] At 20 K, and at the limit of low pressure, MESMER predicts $k \sim 10^{-11}$ cm^3 molecule^{-1} s^{-1} or ~ 10% of the collision rate, providing evidence that the reaction can proceed quickly in those regions of space where both species have been observed. For OH + methyl-ethyl ketone, $CH_3C(O)C_2H_5$, the enhancement in the rate coefficient was not as dramatic, with $\frac{k_{93K}}{k_{295K}} = 72$, and the pressure dependence was not studied.

4.5. Reactions of OH with formaldehyde

The reaction of OH with formaldehyde, H_2CO, was only very recently studied at very low temperatures in the range 22-107 K, using a novel rotating slot to generate a pulsed flow through a Laval nozzle,[18] with $\frac{k_{22K}}{k_{298K}} \sim 13$ and $\frac{k_{22K}}{k_{107K}} \sim 5$.[37] As seen in Figure 4, there was already evidence from measurements between T=200-400 K for the rate coefficient beginning to increase at lower temperatures, and the reaction only possesses a small activation barrier (~2.6 kJ mol^{-1}, similar to the collision energy at 300 K). An increase was calculated using quasi-classical trajectory (QCT) calculations on an ab initio potential energy surface including long-range dipole-dipole interactions. Although at very low temperatures there is insufficient collision energy to surmount the activation barrier, coupling from the reagents' zero point energy into other degrees of freedom as well as quantum effects were suggested to be important.[37] Although no products were measured, the QCT calculations indicate that HCO is the sole product at low temperatures, an important precursor in space for the formation of COMs.

4.6. Reactions of OH with esters

The kinetics of H-atom transfer reactions of OH with L-alanine ethyl ester (T=60-113K)[38] and methyl formate, $CH(O)OCH_3$ (T=22-64K)[39] have been studied in separate Laval nozzle apparatuses.. Methyl formate has been observed in a wide variety of ISM molecular clouds,[39] and its reaction with OH may lead to a number of COMs, but until recently the reaction had not been studied below 233 K. For L-alanine ethyl ester $\frac{k_{60\,K}}{k_{298\,K}}=18$, whereas for methyl formate $\frac{k_{22\,K}}{k_{298\,K}} \sim 600$ and $\frac{k_{22\,K}}{k_{64\,K}} \sim 10$ as shown in Figure 4. For methyl formate, the potential energy surface possesses some pre-reactive complexes with significant binding energies followed by appreciable barriers to reaction. The pressure dependence of this reaction was not measured, nor the products quantified, and so it is not possible to discriminate between collisional stablization of these adducts or tunnelling through the barrier to explain the rapid increase in k at lower temperatures. However, tunnelling was calculated to make a major contribution to the reaction at 298 K,[39] and so is likely to be even more important at low temperatures.

5. SUMMARY AND OUTLOOK

For all molecules considered, the rate coefficient with OH displays a marked negative temperature dependence below 200 K, where previously no kinetic data had existed. As shown in Figure 4, in some cases the value of $\frac{k_{\mathrm{lowT}}}{k_{298\,\mathrm{K}}}$ approaches 1000. The transition temperature (T_r) at which the behaviour switches from normal Arrhenius to a strongly negative dependence of *k* with *T* depends on the VOC, but usually occurs at tropospheric temperatures. Broadly speaking, T_r decreases as the binding energy of the complex increases between 200 and 300 K. . For some reactions, there is no pressure dependence of *k*, suggesting that tunnelling alone accounts for the enhanced rate at low *T*, supported in some cases by direct or indirect evidence of product formation. For other reactions, *k* is pressure dependent at very low temperatures, indicating collisional stabilization of the pre-reactive complex, but with a significant intercept observed at [M]=0 providing evidence also for tunnelling. The pressure affects the extent of the stabilization of the complex, which in turn affects the probability of tunneling, which is controlled not only by the imaginary frequency of the motion associated with tunneling, but also by the barrier height. For an energetic complex, the probability of tunneling will be smaller than for a completely stabilized complex. The complex lifetime is determined by the density of vibrational states, hence for a given temperature, complexes for larger molecules will have longer lifetimes (e.g. 10^{-3} s at 93 K for acetone) and so the enhancement of *k* is more likely due to collisional stabilization, whereas for a small molecule like CH_3OH the lifetime is shorter (2×10^{-7} s at 93 K), and the rate coefficient is dominated by tunneling to form product. However, pressure dependent measurements using a Laval nozzle are very challenging and further studies are needed. Many reactions of OH with VOCs have more than one thermodynamically allowed channel to products, and astrochemical networks require knowledge of the channel yields at very low temperatures in order to calculate molecular abundances in space. Although products have been identified in Laval nozzle experiments for some reactions using laser-induced fluorescence spectroscopy,[8] mass spectrometry[40] or chirped microwave spectroscopy,[41] the determination of absolute product yields is particularly difficult, and is a priority for future work. It would be highly desirable to observe the production and removal of the pre-reactive complex in real time during the reaction. If tunnelling were responsible for the increase in *k*, a marked kinetic isotope effect is expected for H-atom transfer reactions, and although difficult, experiments with deuterated reagents should be attempted in Laval nozzle experiments.

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The author declares no competing financial interest.

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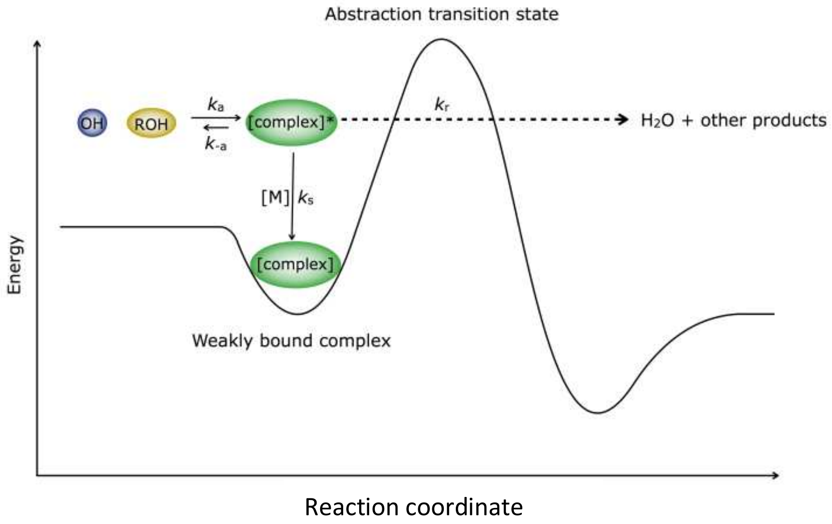

Figure 1. Generic potential energy surface for reaction of OH with an oxygenated volatile organic compounds (here indicated by an alcohol, ROH), showing the pathways available to the weakly bound complex. Reproduced with permission from ref [6]. Copyright 2015 American Chemical Society.

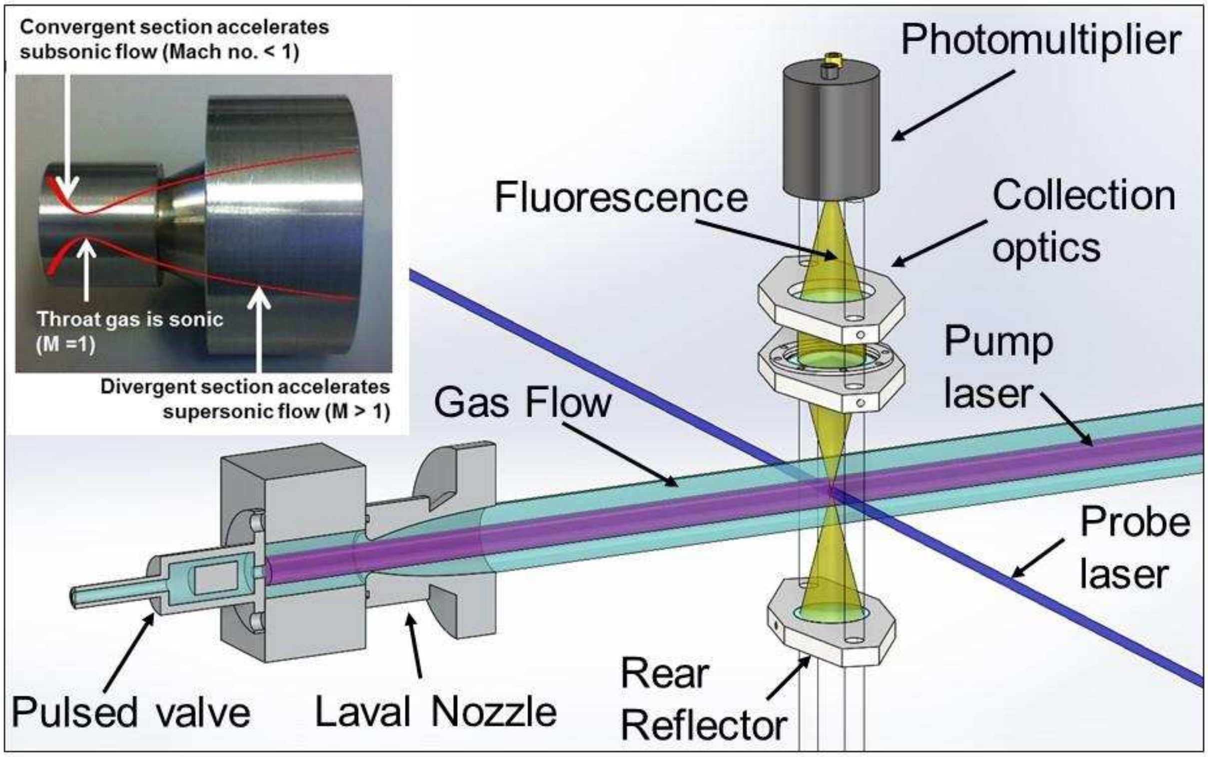

Figure 2. Schematic of a Laval nozzle apparatus for kinetics studies.

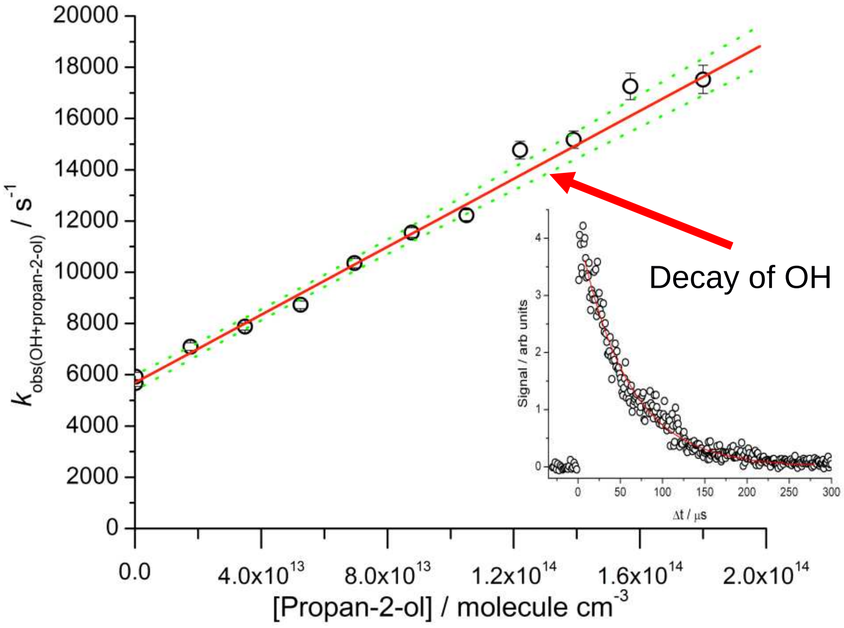

Figure 3. Inset: Temporal decay of OH radicals in the presence of an excess of propan-2-ol at 91±4 K, to which equation (E2) is fitted yielding k_{obs}. Main panel: Variation of k_{obs} with [propan-2-ol] (points), together with a linear fit (red line, ±2σ green dashed line), which yields the bimolecular rate coefficient, k. Adapted with permission from ref [6]. Copyright 2015 American Chemical Society.

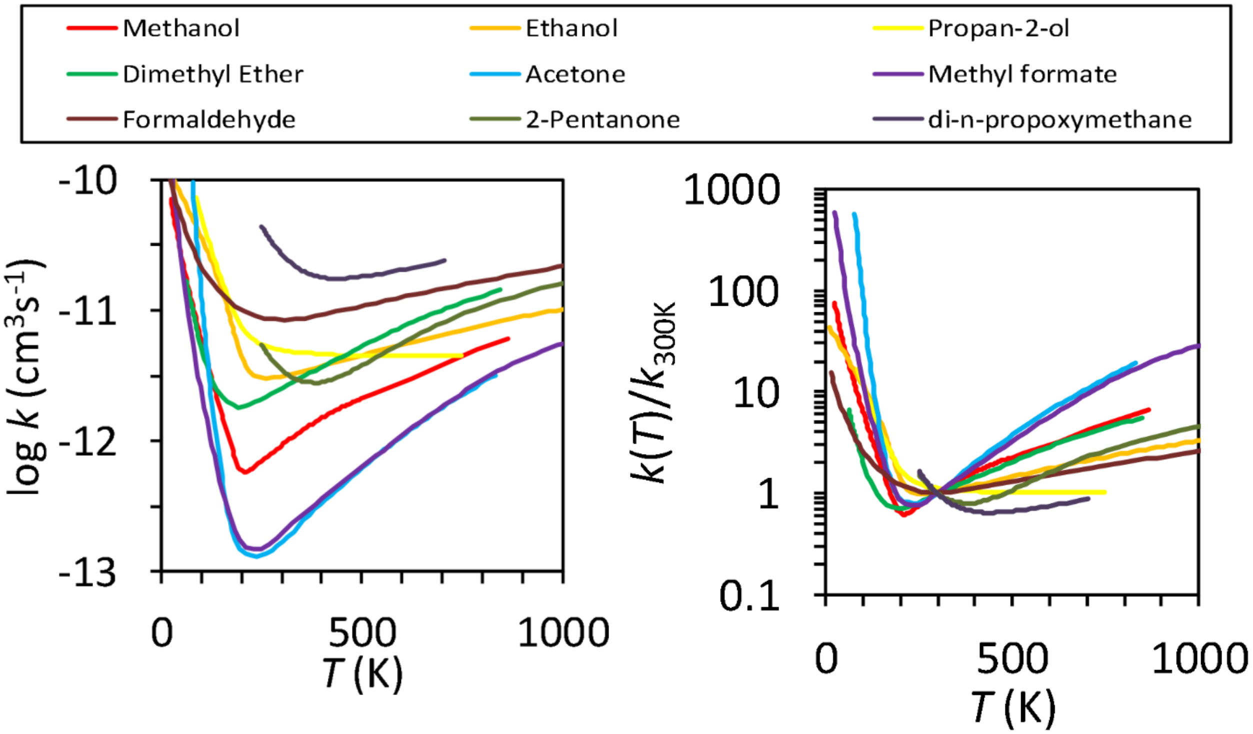

Figure 4. Rate coefficients, *k* (left) and the ratio *k*(*T*)/$k_{300\text{K}}$ (right) as a function of temperature for reaction of OH with a number of oxygenated VOCs. The lines represent interpolated fits to available data in the literature.

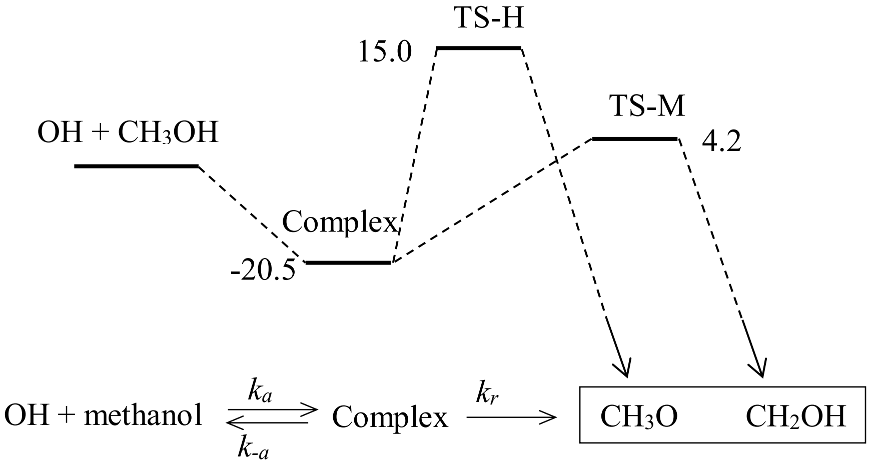

Figure 5. Potential energy surface for the reaction of OH with methanol, with energies in kJ mol^{-1} relative to the reagents. Adapted with permission from ref [8]. Copyright 2013 Nature Publishing Group.

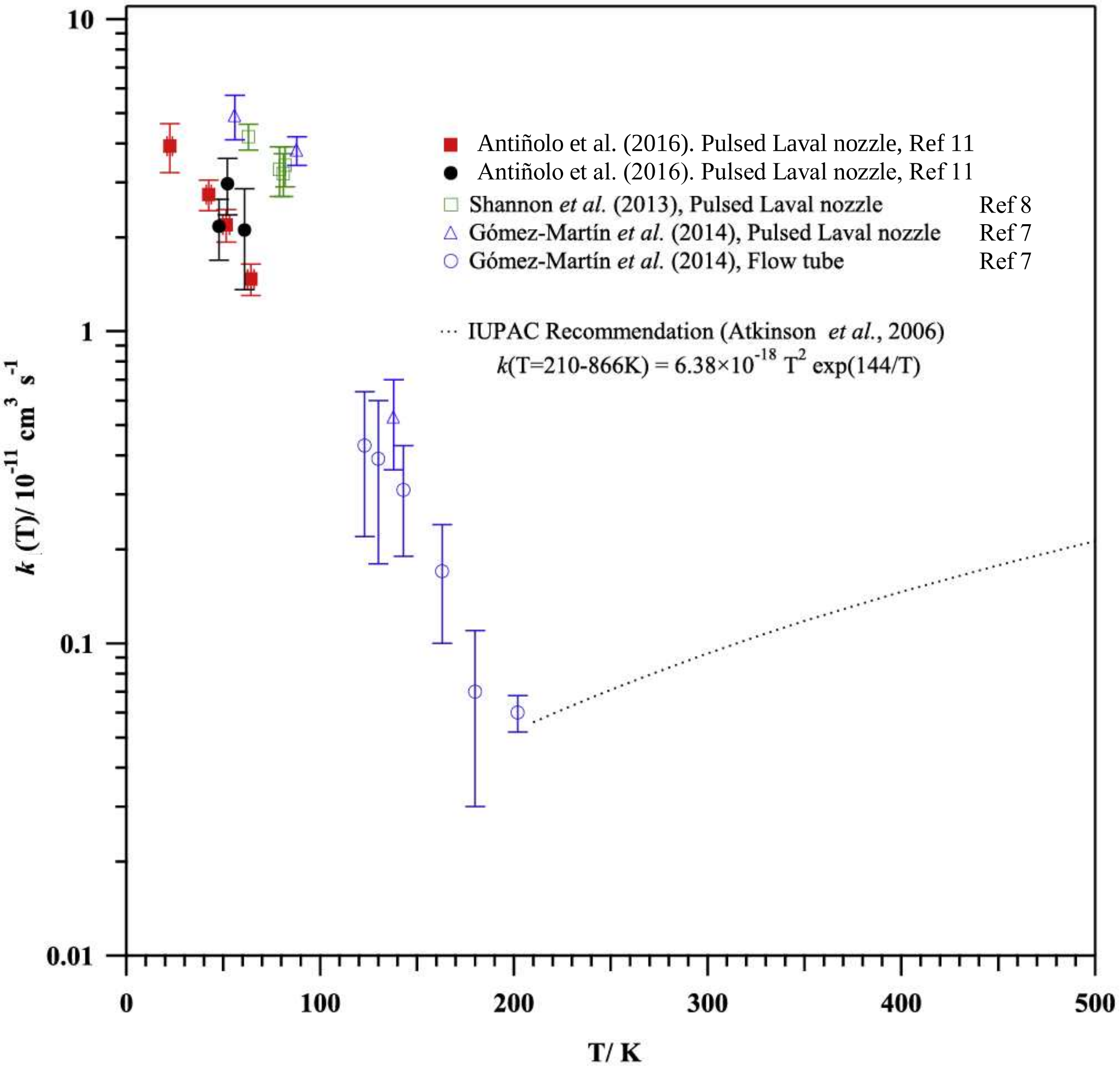

Figure 6. Temperature dependence of the rate coefficient, *k*($OH+CH_3OH$). Adapted with permission from ref [11]. Copyright 2016 American Institute of Physics.

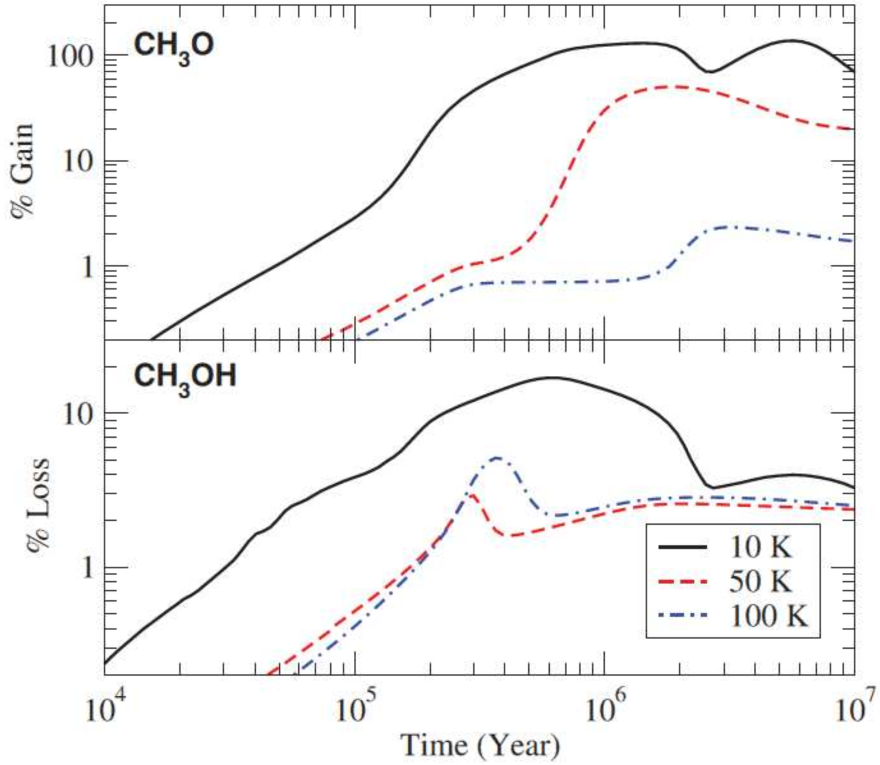

Figure 7. The gain of CH_3O and loss of CH_3OH calculated using a gas-grain model for conditions typical of a dense molecular cloud when the reaction $OH+CH_3OH \rightarrow CH_3O+H_2O$ is included. Reproduced with permission from ref [31]. Copyright 2015 Wiley.

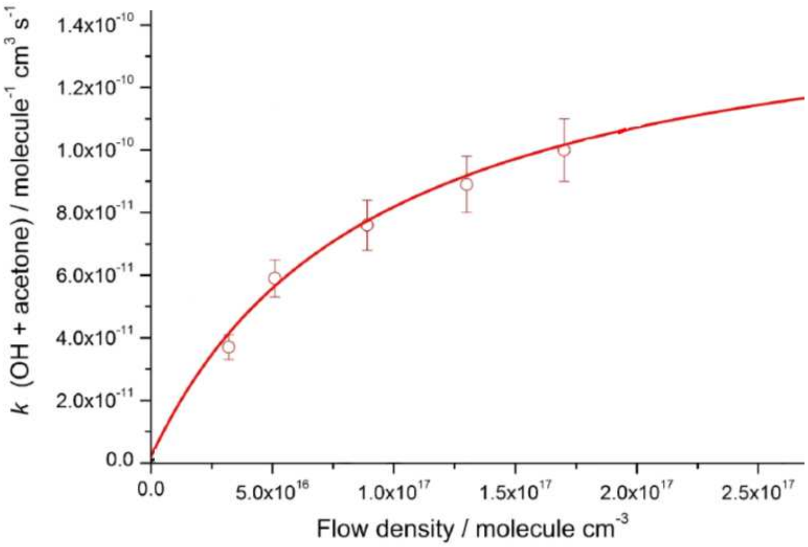

Figure 8. Pressure dependence of *k*(OH + acetone) at ~80 K (red circles, 2σ errors) plotted alongside MESMER Master Equation calculations. Reproduced with permission from ref [9]. Copyright 2014 Royal Society of Chemistry.

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