Comment on "Methanol dimer formation drastically enhances hydrogen abstraction from methanol by OH at low temperature" by W. Siebrand, Z. Smedarchina, E. Martínez-Núñez and A. Fernández-Ramos, Phys. Chem. Chem. Phys., 2016, 18, 22712

R.J. Shannon, J.C. Gómez Martín, R.L. Caravan, M.A. Blitz, J.M.C. Plane,
D.E. Heard, M. Antiñolo, M. Agundez, E. Jiménez, B. Ballesteros, et al.

Comment on "Methanol dimer formation drastically enhances hydrogen abstraction from methanol by OH at low temperature" by W. Siebrand, Z. Smedarchina, E. Martínez-Núñez and A. Fernández-Ramos, *Phys. Chem. Chem. Phys*., 2016, 18, 22712

R. J. Shannon[1,†], J. C. Gómez Martín[1], R. L. Caravan[1,#], M. A. Blitz[1,2], J. M. C. Plane[1,2], D. E. Heard[1,2] *

[1] School of Chemistry University of Leeds, Leeds, LS2 9JT, UK

[2] National Centre for Atmospheric Science, University of Leeds, Leeds, LS2 9JT, UK

M. Antiñolo[3,4], M. Agúndez[5], E. Jiménez[3,4], B. Ballesteros[3,4], A. Canosa[6], G. El Dib[6], J. Albaladejo[3,4], J. Cernicharo[5]

[3] Facultad de Ciencias y Tecnologías Químicas, Departamento de Química Física, Universidad de Castilla-La Mancha, Avda. Camilo José Cela, 1B, Ciudad Real 13071, Spain

[4] Instituto de Investigación en Combustión y Contaminación Atmosférica. Universidad de Castilla-La Mancha. Camino de Moledores s/n. 13071, Ciudad Real, Spain

[5] Instituto de Ciencia de Materiales de Madrid. Consejo Superior de Investigaciones Científicas. C/ Sor Juana Inés de la Cruz, 3. 28049, Cantoblanco (Madrid), Spain

[6] Institut de Physique de Rennes, UMR6251 CNRS-Université de Rennes 1, Département de Physique Moléculaire. Université de Rennes 1. Campus de Beaulieu, Bât 11C, 263 Avenue du Général Leclerc. 35042, Rennes Cedex, France

* Corresponding author. Email: d.e.heard@leeds.ac.uk

† *Now at Department of Mechanical Engineering, Stanford University, 452 Escondido Mall, Stanford, CA 94305, USA, and School of Chemistry, Cantock's Close, University of Bristol, Bristol, BS8 1TS, UK*

*Now at Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA*

Abstract

The article "Methanol dimer formation drastically enhances hydrogen abstraction from methanol by OH at low temperature" proposes a dimer mediated mechanism in order to explain the large low temperature rate coefficients for the OH + methanol reaction measured by several groups. It is demonstrated here theoretically that under the conditions of these low temperature experiments, there are insufficient dimers formed for the proposed new mechanism to apply. Experimental evidence is also presented to show that dimerization of the methanol reagent does not influence the rate coefficients reported under the conditions of methanol concentration used for the kinetics studies. It is also emphasised that the low temperature experiments have been performed using both the Laval nozzle expansion and flow-tube methods, with good agreement found for the rate coefficients measured using these two distinct techniques.

1. Introduction

In their article "Methanol dimer formation drastically enhances hydrogen abstraction from methanol by OH at low temperature"[1] the authors, henceforth referred to as SSNR, propose a new theoretical methanol-dimer mediated mechanism to explain the large low temperature rate coefficients for the OH + methanol reaction measured by several groups (Antiñolo et al. [2]; Gómez Martín et al.[3] and Shannon et al.[4]) with specific reference made to the measurements from Leeds[3, 4]. Hence SSNR call into question the interstellar importance of the OH + methanol reaction occurring in the gas phase.[5]

In this comment we provide theoretical evidence that there are insufficient methanol dimers formed under the conditions used in the kinetic experiments for the SSNR mechanism to occur. Also, a point overlooked by SSNR is that there is good agreement for the low temperature OH + methanol rate coefficients measured using *two* independent experimental techniques, providing evidence that dimer formation is not artificially enhanced through using a Laval expansion based technique. It is also noted that SSNR only use the MPWB1K level of theory in their calculations. While the variational and dynamical calculations performed necessitated the use of a cheaper level of theory, in this Comment we have benchmarked the dimer binding energy against higher level CCSD(T)-F12 calculations and also considered a comprehensive study of the dimer binding energy performed previously by Heger et al. [11] We also provide experimental evidence that the rate coefficients for this reaction are measured at concentrations of methanol which are smaller than those for which the onset of dimerization is observed.

2. Kinetic Model

In order to assess the kinetics of methanol dimer formation, calculations were performed using the

MESMER[6] (Master Equation Solver for Multi Energy well Reactions) software package and using the ro-vibrational properties of methanol and the methanol dimer that were calculated by SSNR at the MPWB1K/6-31G(d,p) level of theory. To give a better description of the ro-vibrational densities of states of the species involved we have treated the hindered rotational modes corresponding to the counter-rotation of the two methanol moieties in the dimer and the various CH_3 internal rotations in the dimer and methanol respectively. Relaxed potential scans were performed about the corresponding dihedral angles using the MPWB1K/6-31G(d,p) level of theory to be consistent with SSNR, and this motion was projected out of the MPWB1K/6-31G(d,p) frequencies to yield a new set of vibrational frequencies as described by Sharma *et al*.[7] This work flow for the treatment of hindered rotation within MESMER has been used many times previously.[8]

In the MESMER calculations we refine the well depth of the dimer through CCSD(T)-f12[9] calculations performed using Molpro[10] , giving a zero-point energy corrected well depth of 18.78 kJ mol^{-1}, i.e. somewhat smaller than the 20.08 kJ mol^{-1} of SSNR[1]. A comprehensive study on the binding energy of the methanol dimer by Heger et al. [11] gives a best estimate for the well depth of 18.3 kJ mol^{-1}, in good agreement with our CCSD calculations.

Energy transfer was modelled with an exponential down model parameterized with an average energy removed per collision $<\Delta E_{down}>$ of 300 cm^{-1}, a value typical of small reaction systems in an N_2 bath gas.[12] In order to perform these calculations, second order rate coefficients were calculated for the dimerization reaction using the recently developed, second order methodology within MESMER[13]. For these calculations a high pressure limiting rate coefficient of 3×10^{-10} cm^3 molecule^{-1}s^{-1} was assumed for the barrierless reaction.

To give reasonable error bars for the master equation calculations it was identified that the most sensitive parameter with respect to dimer formation kinetics is the binding energy of the dimer relative to the separated methanol moieties. A comprehensive review of the binding energies of the methanol dimer recently gave a range of energies between 20.6 and 16.2 kJ mol^{-1} for different high levels of theory.[11] The largest of these binding energies (20.6 kJ mol^{-1}) gives the fastest dimerization rate within the above range of energies. We assigned error bars for the rate by comparing MESMER calculations using the CCSD(T) binding energy of 18.78 kJ mol^{-1} with MESMER calculations using the 20.6 kJ mol^{-1} binding energy and assuming the error bars to be symmetric.

We defined the fraction of methanol monomer, $f_{methanol}$, as follows:

$$f_{methanol} = \frac{[methanol]}{[methanol]_0}$$

Equation (1)

where [methanol]$_0$ is the starting methanol concentration and [methanol]$_0$ = [methanol] + 2[dimer] at every time point. Time profiles of f_{methanol} were obtained from the calculated second-order rate coefficients using the following expression:

$$f_{methanol} = \frac{1}{1+2k_{dimer}[\text{methanol}]_0 t} \qquad \text{Equation (2)}$$

where k_{dimer} is the second-order rate coefficient for dimer formation and t is the reaction time. Equation (2) can be used to calculate the dimer fraction, defined by $f_{dimer} = 0.5(1 - f_{methanol})$. It is noted that Equation (2) does not account for dissociation of the dimer back to monomers and thus at higher temperatures the calculated f_{methanol} will be a lower limit. We have performed calculations both for the conditions within the convergent-divergent region of a Laval nozzle, and for the conditions within the stable flow region after the Laval nozzle used for the Leeds kinetics measurements, and these regions will be discussed in turn.

3. Dimerization fraction within the convergent-divergent region of a Laval nozzle

SSNR raise the question of the possibility of dimer formation within the Laval nozzles themselves prior to the establishment of stable flow. This argument will of course not apply to the flow tube experiments since this is not an expansion technique. Since SSNR do not specify a region of the expansion where clustering may occur prior to establishment of a stable flow, we have mapped the evolution of temperature and pressure from the throat of the Laval nozzle to the establishment of the uniform flow for a 52 K nozzle used by Antiñolo et al.[2] This is a lower temperature expansion than used in Leeds and therefore it should present an upper limit to the amount of clustering compared to the Laval nozzle measurements at 138 K. This nozzle is also representative of that used in Leeds at 56 K because the total densities within these two supersonic flows are very similar. Mapping the properties of the flow was made possible because the Mach number evolution can be derived in the process of calculating the geometry of the walls of the aforementioned 52 K nozzle. For this, we took advantage of a report by Owen and Sherman[14] who developed a bi-dimensional model in order to perform a perturbation calculation of the velocity components and its derivatives of the flow conditions at the throat of the Laval nozzle. To do so, Owen and Sherman used a linearization of the equation of the isentropic and irrotational flow of a perfect gas which leads to the determination of the Mach number step by step along the expansion axis.[15] Once the Mach number is locally known, velocity, temperature, pressure and density can be obtained straightforwardly using the Saint-Venant relation and the isentropic nature of the expansion.[16] The expansion time can be determined as well at every position because the velocity is locally known. In the present case, expansion from the throat to the nozzle exit lasts for about 140 µs. This method has been used since the birth of the CRESU technique in the early 1980s[15] for the design of several tens of Laval nozzles. Agreement between the predicted temperature at the nozzle exits and the

measured ones were always found to be very good, within typically a 2% difference. This accuracy is also expected along the expansion flow inside the divergent section of the Laval nozzle.

Since the speed of the gas flow is known at each point, Equation (2) can be modified to calculate the dimer fraction as follows:

$$df_{dimer} = 0.5 * (1 - \frac{1}{1 + 2k_{dimer}(t)[methanol]_0(t)dt})$$ Equation (3)

where $k_{dimer}(t)$ and $[methanol]_0(t)$ are functions of time within the nozzle and $[methanol]_0(t)$ depends not only upon the evolution of conditions within the nozzle, but also upon the total f_{dimer} for times $t' < t$ in the nozzle. df_{dimer} was determined at discrete points along the nozzle and then integrated numerically to give f_{dimer}. A total of 248 quadrature points were used in this integration. These calculations predict f_{dimer} is proportional to $[methanol]_0$, and it is not apparent how SSNR's assumed constant f_{dimer} of 0.3 can be reconciled within the kinetic model for dimerization. The largest $[methanol]_0$ used in the 52 K rate coefficient determination described by Antiñolo et al[2] was 0.5% of the total gas flow. Assuming this $[methanol]_0$, the predicted f_{dimer} is only 0.036±0.021 by the end of the nozzle axis, and if the $[methanol]_0$ is reduced to 0.1 % of the total flow the predicted f_{dimer} is reduced to 0.007±0.004. It is also noted that Equation (3) overestimates the degree of dimerization at higher temperatures since it does not account for re-dissociation of the dimer back to methanol. Figure 1 displays the change in df_{dimer} as a function of distance z along the nozzle axis for both 0.5% and 0.1% methanol. It should also be highlighted that the most favorable conditions for dimerization occur at the very end of the nozzle, at the lowest temperatures where stable flow has been established.

4. Dimerization under experimental conditions used to determine rate coefficients

The results from Section 3 demonstrate that little dimerization occurs within the expansion region of the Laval nozzles and that the optimum conditions for dimer formation are obtained once the stable flow has been established. For completeness (and also to consider the flow tube kinetics experiments), we have performed similar MESMER calculations for conditions corresponding to those encountered during the two low temperature rate coefficient measurement studies referred to by SSNR. The values of f_{dimer} are shown in Table 1 and correspond to both the stable-flow region of the Laval nozzle and the conditions of the flow tube experiments. f_{dimer} is calculated after 300 μs and 1 ms flow-time which are representative of the times over which the kinetics were monitored for the Laval nozzle and the flow tube experiments, respectively. These results demonstrate that even when the equilibrium $f_{methanol}$ is close to zero (i.e. f_{dimer} ~0.5), the calculated f_{dimer} in the kinetics experiments is considerably smaller, showing that the timescale for establishment of this equilibrium is much longer than the window over which the kinetics experiments

were performed. At all but the lowest temperatures, dimer formation is negligible even at the very end of the reaction window. It is also clear that f_{dimer} is strongly dependent upon [methanol]$_0$, which is incompatible with the model proposed by SSNR. It is noted that in some cases the errors for f_{dimer} in Table 1 are larger than the values of f_{dimer} themselves, which is purely due to the method by which the errors were determined using a range of dimer binding energies as outlined in Section 2. Under conditions where the equilibrium f_{dimer} is near zero, f_{dimer} is particularly sensitive to the binding energy of the dimer, hence the large errors. However, even considering the error limits, the f_{dimer} values are significantly lower than those used by SSNR even at the lowest temperature.

The results in Table 1 do not include the small amount of dimerization predicted to occur within the Laval nozzle itself and which were calculated in Section 3. We now consider the cumulative effect of dimerization both within the convergent region of a Laval nozzle and the stable flow region. Figure 2 shows f_{dimer} as a function of time throughout a kinetics experiment performed using the Laval nozzle at the lowest temperature of 56 K. For the value of f_{dimer} at $t = 0$ (the beginning of the time-window for the kinetics experiment in the Laval stable flow region) we use the calculations within the convergent-divergent region of the Laval nozzle presented in Section 3 above. Figure 2 shows the calculation of f_{dimer} at both the smallest and largest [methanol]$_0$, and in both cases f_{dimer} is well below the value of 0.3 assumed by SSNR. Furthermore, f_{dimer} is not constant but can be observed to increase with time.

5. Experimental indications of clustering

The above theoretical analysis demonstrates that under the conditions of the low temperature experiments assuming thermal kinetics, the formation of a significant amount of dimers can be ruled out. In addition to the University of Leeds Laval experiments, further Laval experiments have been performed on OH + methanol by Antiñolo et al.[2] at the Universidad de Castilla-La Mancha and at the Université de Rennes 1. The two sets of results are in good agreement and demonstrate that the OH + methanol low temperature rate coefficients are independent of a given Laval nozzle setup. SSNR specifically question whether Laval nozzles themselves promote condensation and cite three principal papers as evidence for this phenomenon [17-19]. While one of the cited papers does involve a Laval nozzle apparatus,[19] the intention of that study is not to produce a medium suitable for kinetic measurements. Rather, the cited study by Laksmono et al. [19] is primarily looking to deliberately induce condensation, and as such they operate their Laval nozzle at far higher pressures than used in more traditional Laval kinetic studies, and their expansion is clearly not stable, with the temperature observed to steadily decrease with distance upon exit of the Laval nozzle. Therefore, the experimental conditions in the work of Laksmono et al. [19] are far removed from the ones used in the work of Shannon,[4] Gómez Martín et al.[3] and Antiñolo et al.[2] The other

papers involve a free jet expansion and are in no way analogous to the thermal conditions within a Laval flow.

The presence of any curvature of bimolecular plots (also known as second order plots) is a well-established marker for dimer formation. [2, 20-23] Unless the dimer concentration is negligible or constant with changing concentration of excess reactant, then a bimolecular plot will necessarily exhibit curvature. This can go one of two ways; an upward curvature would indicate dimer formation but with the dimer reacting significantly more quickly with OH compared with the monomer as proposed by SSNR. On the other hand, a downward curvature would indicate the removal of methanol via dimerization (so it is no longer available for reaction with OH) and the methanol dimer reacting at a similar rate or slower with OH compared with the monomer. SSNR propose that the dimer concentration is constant over the range of [methanol] used in the experiments of Gómez-Martín et al.[3] However, the theoretical results presented in this comment demonstrate that this is not the case. Experimentally, curvature has been reported in two studies of the reaction of OH with methanol using pulsed Laval nozzles.[2,3] Antiñolo et al. [2] observed distinct downward curvature at T = 22.4 K for $[methanol]_0 > 1 \times 10^{14}$ molecule cm^{-3}, as shown in Figure 3 using the Universidad de Castilla-La Mancha Laval nozzle. The corresponding plot at 64.2 K reported by Antiñolo et al.[2] was linear up to the highest $[CH_3OH]$ used, 3×10^{14} molecule cm^{-3}. In addition, Gómez-Martín et al.[3] reported that at the lowest temperature studied with the University of Leeds Laval nozzle system (56 K), the bimolecular plot for this reaction was linear up to around the same concentration (2.5×10^{14} molecule cm^{-3}) above which the plot exhibited downward curvature, as shown in Figure 4. Both of these studies provide strong experimental evidence for the onset of dimerization, but that the reactivity of the dimer towards OH is similar or lower than for methanol itself, and certainly not significantly higher as calculated by SSNR[1].

Great care was taken in both the Laval [2, 4] and flow tube experiments[3] to keep concentrations of methanol low enough that dimerization did not occur. Only the portion of second-order plots that is linear is used to obtain the bimolecular rate coefficient. [2-4] The lack of dimer formation in the OH + methanol system for $[CH_3OH]$ used to obtain rate coefficients is consistent with studies on other OH + oxygenated hydrocarbon systems. It is highly desirable to develop an experimental analytical method which is able to quantitatively detect the dimer directly under the conditions of the low temperature flow, in order to measure the fraction of dimer present, and hence provide evidence to support whether the dimer mechanism is operating or not.

6. Conclusions

In summary, we argue using both theoretical and experiment evidence that the dimer mechanism

proposed by SSNR cannot account for the low temperature Laval Nozzle kinetics observations for the reaction of OH with methanol. Our master equation theoretical model predicts a maximum f_{dimer} of 0.090±0.047 (considerably lower than that assumed by SSNR) considering both dimerization within the Laval nozzle and within the resulting stable flow, and this is only when using the very highest methanol concentrations and at the very end of the time window over which the kinetics were monitored experimentally. For higher temperatures or even just lower methanol concentrations at the lowest temperatures we demonstrate that f_{dimer} quickly becomes negligible. Additionally, even the equilibrium values of f_{dimer} rapidly tend to zero above 120 K. Experimentally, curved bimolecular plots of OH loss rate versus methanol were presented to show the onset of methanol dimerization, but the rate coefficients for OH + methanol are always obtained from the linear portions of these plots where the concentration of methanol is always lower than the onset of any dimer formation. The rate coefficients obtained using the Laval nozzle experiments agree with those obtained by the low temperature flow tube experiments, for which there is no expansion. Direct determination of the minimum monomer concentration of methanol required to detect the onset of dimers would be of great help in order to clarify the experimental and recent theoretical developments.

Conflicts of interest

There are no conflicts of interest to declare.

References

1.   W. Siebrand, Z. Smedarchina, E. Martínez-Nuñez and A. Fernandez-Ramos, *Phys Chem Chem Phys*, 2016, **18**, 22712-22718.

2. M. Antiñolo, M. Agúndez, E. Jiménez, B. Ballesteros, A. Canosa, G. El Dib, J. Albaladejo and J. Cernicharo, *Astrophys J*, 2016, **823,** 25.

3. J. C. Gómez Martin, R. L. Caravan, M. A. Blitz, D. E. Heard and J. M. C. Plane, *J Phys Chem A*, 2014, **118**, 2693-2701.

4. R. J. Shannon, M. A. Blitz, A. Goddard and D. E. Heard, *Nat Chem*, 2013, **5**, 745-749.

5. K. Acharyya, E. Herbst, R. L. Caravan, R. J. Shannon, M. A. Blitz and D. E. Heard, *Mol Phys*, 2015, **113**, 2243-2254.

6. D. R. Glowacki, C. H. Liang, C. Morley, M. J. Pilling and S. H. Robertson, *J Phys Chem A*, 2012, **116**, 9545-9560.

7. S. Sharma, S. Raman and W. H. Green, *J Phys Chem A*, 2010, **114**, 5689-5701.

8. A. J. Eskola, S. A. Carr, R. J. Shannon, B. Wang, M. A. Blitz, M. J. Pilling, P. W. Seakins and S. H. Robertson, *J Phys Chem A*, 2014, **118**, 6773-6788.

9. H. J. Werner, G. Knizia and F. R. Manby, *Mol Phys*, 2011, **109**, 407-417.

10. H. J. Werner, P. J. Knowles, G. Knizia, F. R. Manby and M. Schutz, *Wires Comput Mol Sci*, 2012, **2**, 242-253.

11. M. Heger, M. A. Suhm and R. A. Mata, *J Chem Phys*, 2014, **141,** 101105.

12. A. W. Jasper, C. M. Oana and J. A. Miller, *Proc Combust Inst*, 2015, **35**, 197-204.

13. M. A. Blitz, N. J. B. Green, R. J. Shannon, M. J. Pilling, P. W. Seakins, C. M. Western and S. H. Robertson, *J Phys Chem A*, 2015, **119**, 7668-7682.

14. J. M. Owen and F. S. Sherman, *Engineering Project Report: He 150-104*, 1952.

15. G. Dupeyrat, J. B. Marquette and B. R. Rowe, *Phys Fluids*, 1985, **28**, 1273-1279.

16. E. Jiménez, B. Ballesteros, A. Canosa, T. M. Townsend, F. J. Maigler, V. Napal, B. R. Rowe and J. Albaladejo, *Review of Scientific Instruments*, 2015, **86**, 045108.

17. U. Buck, X. J. Gu, C. Lauenstein and A. Rudolph, *J Chem Phys*, 1990, **92**, 6017-6029.

18. F. Kollipost, J. Andersen, D. W. Mahler, J. Heimdal, M. Heger, M. A. Suhm and R. W. Larsen, *J Chem Phys*, 2014, **141**.

19. H. Laksmono, S. Tanimura, H. C. Allen, G. Wilemski, M. S. Zahniser, J. H. Shorter, D. D. Nelson, J. B. McManus and B. E. Wyslouzil, *Phys Chem Chem Phys*, 2011, **13**, 5855-5871.

20. S. E. Taylor, PhD Thesis, University of Leeds, 2007.

21. R. J. Shannon, PhD Thesis, University of Leeds, 2012.

22. R. L. Caravan, R. J. Shannon, T. Lewis, M. A. Blitz and D. E. Heard, *J Phys Chem A*, 2015, **119**, 7130-7137.

23. S. Hamon, S. D. Le Picard, A. Canosa, B. R. Rowe and I. W. M. Smith, *J Chem Phys*, 2000, **112**, 4506-4516.

Temperature / K	[M] / 10^{16} molecule cm^{-3}	$[methanol]_0$ /10^{15} molecule cm^{-3}	$2k_{dimer}$/ 10^{-13} cm^3 molecule^{-1} s^{-1}	f_{dimer} at smallest $[methanol]_0$	f_{dimer} at largest $[methanol]_0$
56 [*]	4.4	0.07-0.22 [a]	18.18±10.36	$(1.8±0.9)×10^{-2}$ **(5.0±0.0)×10^{-1}**	$(5.3±2.6)×10^{-2}$ **(5.0±0.0)×10^{-1}**
88 [*]	9.4	0.1-0.6	3.86±2.36	$(5.7±3.4)×10^{-3}$ **(1.8±1.9)×10^{-1}**	$(3.2±1.8)×10^{-2}$ **(3.2±1.1)×10^{-1}**
123	3.15	0.3-1.5	0.23±0.15	$(0.4±2.2)×10^{-3}$ **(0.4±2.2)×10^{-3}**	$(0.2±1.1)×10^{-2}$ **(0.2±1.1)×10^{-2}**
138 [*]	7.8	0.1-0.9	0.26±0.18	$(1.6±6.4)×10^{-5}$ **(1.6±6.4)×10^{-5}**	$(1.4±5.8)×10^{-4}$ **(1.4±5.8)×10^{-4}**
143	2.76	0.1-1.6	0.08±0.06	$(0.8±3.2)×10^{-5}$ **(0.8±3.2)×10^{-5}**	$(1.3±5.0)×10^{-4}$ **(1.3±5.0)×10^{-4}**
163	2.46	0.3-1.6	0.06±0.03	$(0.5±0.5)×10^{-5}$ **(0.5±0.5)×10^{-5}**	$(0.8±5.0)×10^{-5}$ **(0.8±5.0)×10^{-5}**

Table 1. Calculated f_{dimer} using MESMER performed for conditions corresponding to kinetics measurements at low temperatures from Gómez-Martín et al.[3] Temperatures with a * indicate that rate coefficients were determined using a Laval nozzle whilst other temperatures correspond to rate coefficients determined using a flow tube. The smallest and largest $[methanol]_0$ for which f_{dimer} is calculated correspond to the extremes in the range of concentrations given in the 3rd column. The calculated values of f_{dimer} are for reaction times of 300 μs and 1 ms corresponding to the reaction window used for the Laval nozzle and flow tube kinetics experiments, respectively. The f_{dimer} values in bold correspond to the equilibrium value under those conditions. [a] Higher values of $[methanol]_0$ were used at 56 K but curvature was observed in the experimental bimolecular plots and hence $[methanol]_0=2.2 ×10^{14}$ molecule cm^{-3} was the largest concentration used in the determination of the rate coefficient reported by Gomez Martin et al. [3]
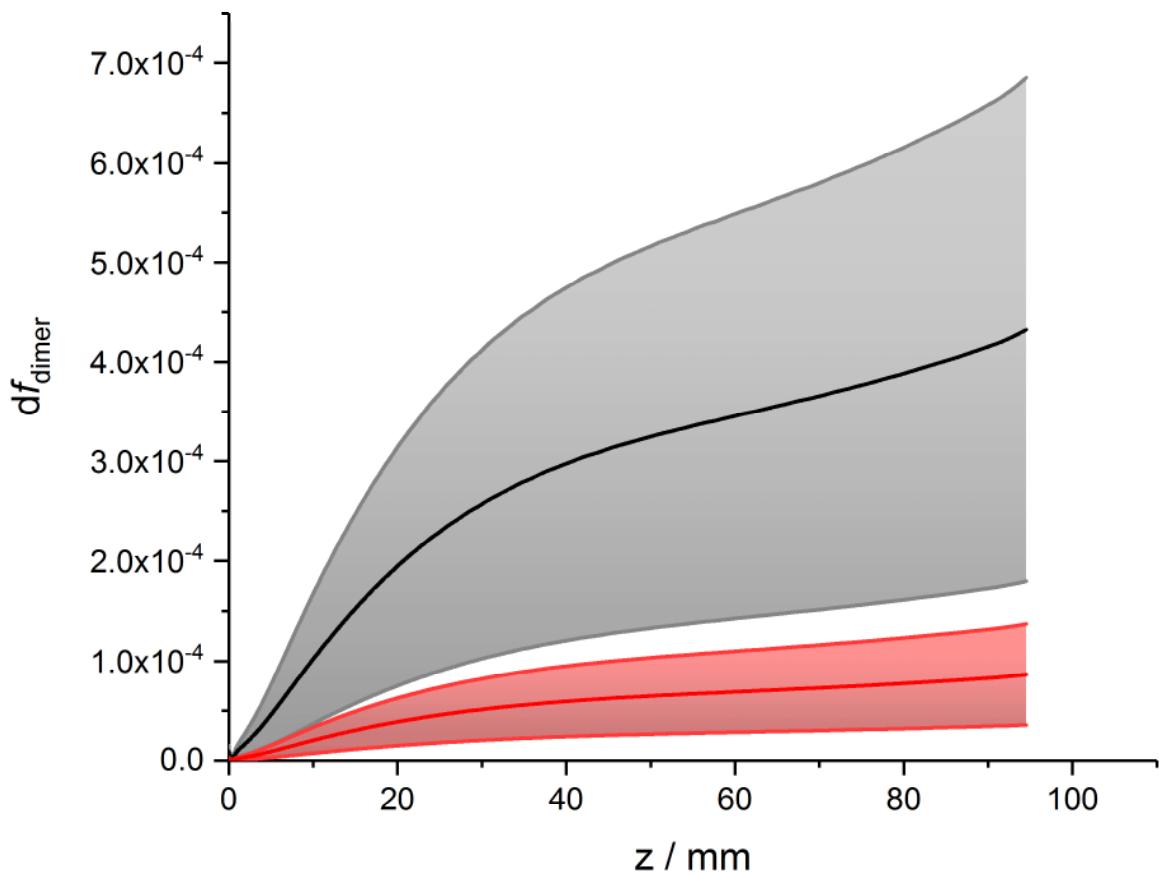
Figure 1. Calculated df_{dimer} as a function of the distance along the 52 K Laval nozzle axis (z) from throat to nozzle exit. The black line assumes 0.5% of the gas flow consists of methanol (the maximum used with this nozzle) whilst the red line assumes 0.1% of the total gas flow consists of methanol. Error bars are assigned through varying the binding energy of the dimer as described in Section 2 of the manuscript.
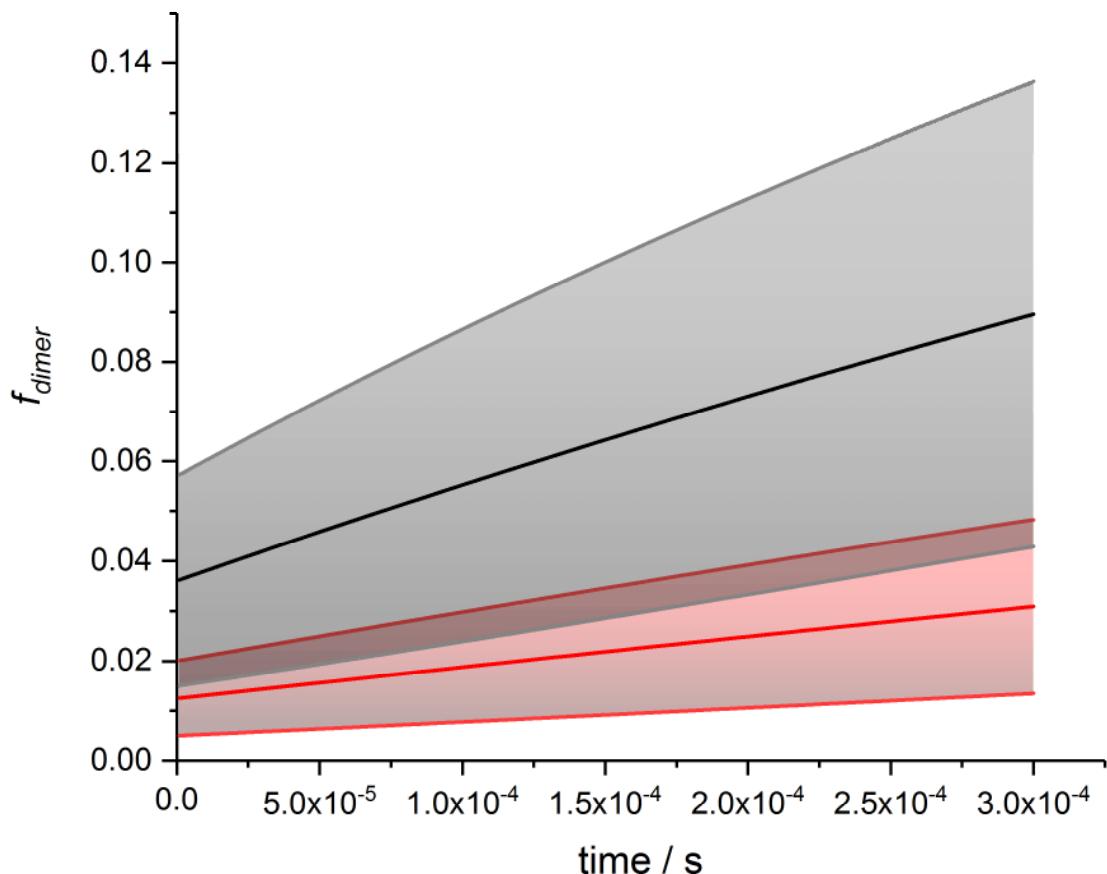
Figure 2. Calculated f_{dimer} as a function of time in the stable-flow region for the 56 K Laval nozzle experiments. The zero time f_{dimer} values are taken from MESMER simulations of dimerization within a 52 K Laval nozzle described in Section 3 and calculated using the appropriate [methanol]$_0$. The black line corresponds to the maximum [methanol]$_0$ of 2.2×10^{14} molecule cm^{-3}, whereas the red line assumes the minimum [methanol]$_0$ of 7×10^{13} molecule cm^{-3}. Error bars are assigned through varying the binding energy of the dimer as described in Section 2 of the manuscript.
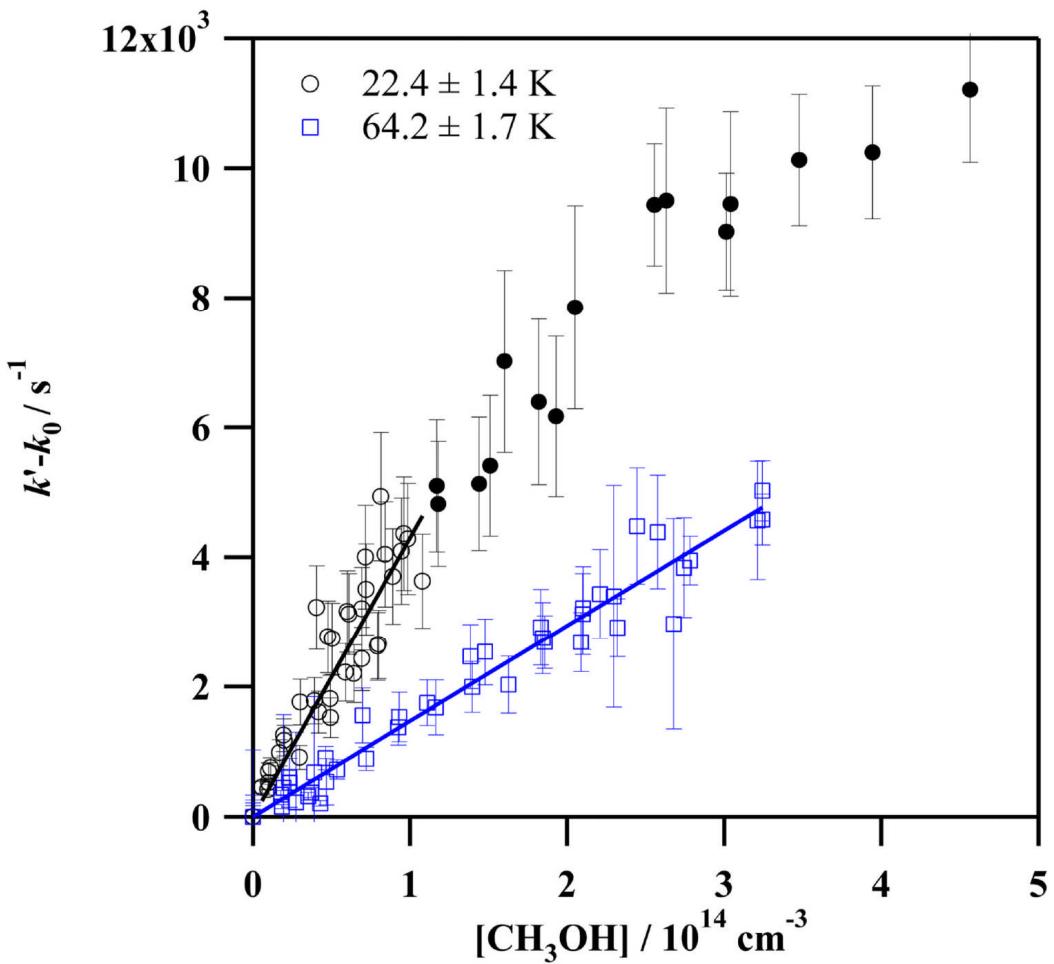
Figure 3. Experimental results of the pseudo-first order loss of OH versus methanol concentration (bimolecular or second order plot) from the Universidad de Castilla-La Mancha Laval apparatus (taken from Antiñolo et al. [2]) at 22.4 K and 64.2 K. The black solid line at 22.4 K is a fit to the linear portion of the data from which the rate coefficient for the reaction of OH with methanol is determined. At 64.2 K the plot is linear over the entire range of [CH₃OH], with the blue line being the fit from which the rate coefficient is determined.
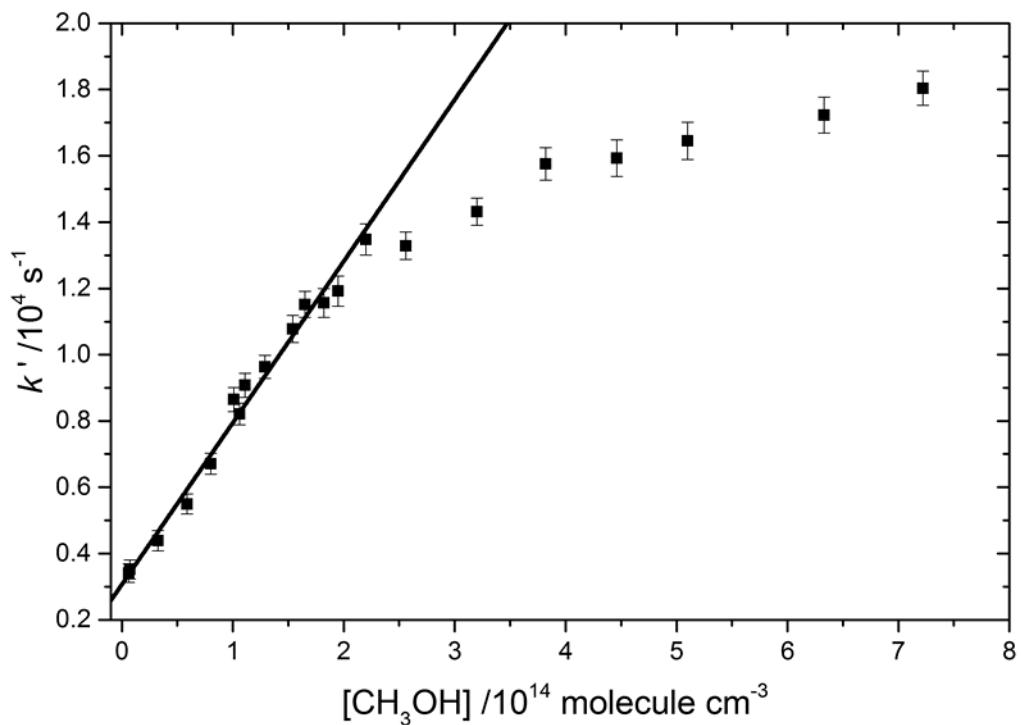
Figure 4. Experimental results (squares) of the pseudo-first order loss of OH (k') as a function of the methanol concentration (bimolecular plot) using the University of Leeds Laval apparatus at 56 K, together with a linear-least squares fit to the linear portion of the data (solid line), from which the bimolecular rate coefficient for the reaction of OH with methanol was determined. The results were reported in Gómez-Martín et al.[3]