Reply to the 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

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We reply briefly to the arguments presented by the authors of the Comment to the article “Methanol dimer formation drastically enhances hydrogen abstraction from methanol by OH at low temperature” (henceforth, we refer to the article as SSNR,[1] as in the Comment). In fact, these arguments are not new to us, as they have been put forward in Refs. 2-4, and most of our answers can be found in_SSNR and in the Supporting Information. However, to emphasize the fact that we fully stand behind the conclusions in SSNR, we address at some length the main two arguments of the Comment, which concern: (i) the binding energy of the methanol dimer and its influence on the dimerization rate constant; and (ii) the dependence of the pseudo-first order rates on the methanol concentration.

(i) The binding energy of the methanol dimer and its influence on the dimerization constant

The best theoretical estimate for the binding energy of the methanol dimer[5] is 18.3 kJ·mol^{-1}. The MPWB1K/6-31G(d,p) calculations in SSNR yield a value of 20.1 kJ·mol^{-1} (not 23.6 kJ·mol^{-1}, as stated in the Comment), so this value is still in the range between 18.8 and 20.6 kJ·mol^{-1} for which the master equation calculations described in the Comment were performed. It is argued that SSNR overestimates the binding energy and, as a consequence, the dimerization rate constant, k_{dimer}.

It is also indicated that k_{dimer} has a direct impact on the fraction of methanol dimer, in such a way that a larger value of k_{dimer} translates into a larger fraction of methanol dimer. The calculations performed in the Comment list a value of $k_{\mathrm{dimer}} = 9.1 \times 10^{-13}$ cm^3·molecule^{-1}·s^{-1} at the lowest reported temperature of 56 K and of 3.0×10^{-15} cm^3·molecule^{-1}·s^{-1} at the highest reported temperature of 163 K. However, on the basis of previous experimental values of dimerization constants for other systems using the Laval nozzle technique and on our own calculations, we conclude that the dimerization constants reported in the Comment are unphysically low. As an example, their value is about 20 times smaller than the measured dimerization constant of benzene (a nonpolar molecule) by Hamon et al.[6] ($k_{\mathrm{dimer}} = 2.2 \times 10^{-11}$ cm^3·molecule^{-1}·s^{-1} at 49.1 K). These authors performed the same type of Laval nozzle experiments using a benzene concentration of 1.75×10^{14} molecules·cm^{-3}. This benzene concentration is within the interval of the methanol concentration used in the Comment, which is between 0.7×10^{14} and 2.2×10^{14} molecules·cm^{-3}. Taking into account that the experimental dimerization constant for benzene[7] is at most 12 kJ·mol^{-1}, it seems highly unlikely that for methanol k_{dimer} would be so small. To probe this, we have_carried out new calculations of k_{dimer} using the analytical potential energy surface of Ref. 8 employed in the quasiclassical calculations performed in SSNR. This analytical potential energy surface provides a binding energy of 18.3 kJ·mol^{-1}, which is slightly lower than the values used in the Comment. To perform these calculations we separated the two methanol molecules by more than 10 Å and followed the gradient using the Page-McIver algorithm in Cartesian mass-scaled coordinates with a stepsize of 0.0012 a_o and Hessian calculations every

25 steps. The dimerization rate constants, $k_{\mathrm{dimer}}^{\mathrm{ICVT}}$, were calculated using the improved canonical variational transition state theory (ICVT).[9] The reaction is barrierless, but the activation free energy can be easily evaluated at each of the points along the reaction path for which the Hessian is available. At a given temperature, the bottleneck for reaction corresponds to the value of the reaction path for which the free energy of activation has a maximum. The values of $k_{\mathrm{dimer}}^{\mathrm{ICVT}}$ are 1.1×10^{-10} and 7.8×10^{-11} $\mathrm{cm}^3 \cdot \mathrm{molecule}^{-1} \cdot \mathrm{s}^{-1}$ at 56 K and 163 K, respectively. These values are more than two orders of magnitude higher than the values reported in the Comment. Therefore, we conclude that the calculations of the Comment seriously underestimate the dimer fraction.

Additionally, the Comment mentions that SSNR assumed a dimer fraction of 30%. This value (called α in SSNR) refers to the fraction of the equilibrium concentration (denoted as y_{eq} in SSNR). Thus, the dimer fraction (called f_{dimer} in the Comment) is 0.15 at the lowest temperatures and not of 0.30, as stated in the Comment. This value can be easily checked from the values of Table 1 and from Eq. 3 of SSNR.

(ii) The dependence of the pseudo-first order rates on the methanol concentration.

The Comment states that "The presence of any curvature of bimolecular plots (also known as second order plots) is a well-established marker for dimer formation." However, that assertion does not rest on direct experimental evidence, but on empirical plots, and we consider that the following arguments posed in SSNR are still valid: (ii.a) The reaction of methanol monomer with OH is too slow to explain the low-temperature and low-pressure Laval nozzle experiments; (ii.b) Linear pseudo-first order plots do not prove the absence of methanol dimers and other small clusters.

In fact, a very recent publication[10] on the reaction of methanol monomer with OH carried out with state-of-the-art electronic structure calculations has confirmed (ii.a). At the conditions of the Laval nozzle experiment (low pressure), the calculated thermal rate constant at 50 K is more than two orders of magnitude smaller than the experimental value. That work clearly indicates that it is not possible to reproduce the experimental values without partial stabilization of the pre-reactive complex. Two possible ways of stabilizing the complex are: (1) to work under high-pressure conditions or (2) to have the participation of a third body. Since the Laval experiments are performed at low pressure, the most plausible explanation, which also matches the experimental data, is to assume that methanol dimers provide the needed third body to stabilize the complex and to speed up the reaction. The Comment states that, if there are methanol dimers, they will be less reactive than methanol monomers because of the downward curvature of the pseudo-first order plot. However, that affirmation rests on very weak evidence; the only serious attempt to evaluate the reactivity of methanol dimers toward OH has been reported in SSNR and that work concludes that methanol dimers are about two orders of magnitude more reactive than methanol monomers. This result raises a new question, how is then possible that the plots are linear at low methanol concentrations and become sublinear at higher concentrations? Our explanation to this question is that at low methanol concentrations dimers and other small cluster (probably trimers and tetramers) are present at a nearly constant dimer fraction. This argument is in the line of the Laval nozzle experiments carried out by Ferreiro et al.[11] who showed that for low (propane) concentration in such beams oligomers are generated and that their average size is nearly steady. This is compatible with Eq. 3 of the SSNR paper and with a linear variation of the pseudo-first order with methanol concentration. At high methanol concentrations, larger clusters and even droplets could be formed. The big clusters are expected to be less reactive towards OH, thus explaining the downward curvature of the plots (see the SI of SSNR). However, in our opinion a further debate on these issues in the literature will be fruitless until new experimental data are available.

Conflicts of interest

There are no conflicts of interest to declare.

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