

Gas phase reaction kinetics of complex organic molecules at temperatures of the interstellar medium: The OH + CH₃OH case

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Abstract. Recent experimental and theoretical works concerning gas-phase radical-neutral reactions involving Complex Organic Molecules are reviewed in the context of cold interstellar objects with a special emphasis on the OH + CH₃OH reaction and its potential impact on the formation of CH₃O.

Keywords. ISM: molecules, astrochemistry, molecular processes

1. Introduction

Complex Organic Molecules (COMs) have been observed in the Interstellar Medium (ISM) for a long time, since the first reported observations by Cummins *et al.* 1986. COMs like CH₃OH, C₂H₅OH, CH₃OCH₃, HCOOCH₃ etc. have been identified and have been found in many interstellar environments since then. Interestingly, for quite a long time, COMs have been observed in lukewarm objects such as hot cores and hot corinos (Bacmann *et al.* 2012; Vastel *et al.* 2014). Grain surface chemistry was claimed to be the source for the synthesis of such species during the warm-up of grains at $T > 30$ K which ensures sufficient mobility of radicals present at the grain surface to recombine and form the mentioned COMs (Garrod & Herbst 2006). These can subsequently desorb to the gas phase at temperatures typically above 100 K.

In contrast, only a few observations of COMs were available in the cold gas environments until recently. Investigations of the dense core Barnard 1b (Öberg *et al.* 2010; Cernicharo *et al.* 2012) and prestellar cores (Bacmann *et al.* 2012; Vastel *et al.* 2014) shed a new light on the mechanisms responsible for the presence of COMs in such cold environments ($T \sim 10$ K) for which the previous mentioned formation process on grains cannot hold. Gas phase reactions, initially left apart, were put back to the scene as possible routes for the formation of COMs in cold environments (Vasyunin & Herbst 2013). At such low temperatures, however, almost nothing is known concerning the rate constants and products issued from potential interesting reactions.

Over the last decade, a great experimental and theoretical effort has been undertaken in order to study the reactivity of neutral radicals with interstellar COMs at very low temperatures.

From an experimental point of view, methanol, ethanol, acetone, dimethylether (DME), methyl formate, formaldehyde, acetonitrile and methyl amines have been investigated in several laboratories (Table 1). All these results have been obtained using CRESU reactors (French acronym for Cinétique de Réaction en Ecoulement Supersonique Uniforme or Reaction Kinetics in Uniform Supersonic Flows), a well-established technique for the study of gas-phase reaction kinetics at very low temperatures (Potapov *et al.* 2017).

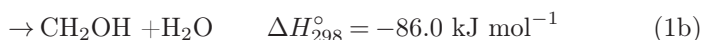
Table 1. Recent experimental studies of radical - COMs reactions including the minimum explored temperature T_{min}

Reaction	T_{min} (K)	References
OH + CH ₃ OH	12	Shannon <i>et al.</i> 2013; Gómez Martín <i>et al.</i> 2014; Antiñolo <i>et al.</i> 2016; Ocaña <i>et al.</i> 2019
OH + C ₂ H ₅ OH	12	Caravan <i>et al.</i> 2015; Ocaña <i>et al.</i> 2018
OH + CH ₃ C(O)CH ₃	12	Shannon <i>et al.</i> 2010; Shannon <i>et al.</i> 2014a; Blázquez <i>et al.</i> 2019
OH + CH ₃ OCH ₃	63	Shannon <i>et al.</i> 2010; Shannon <i>et al.</i> 2014a
OH + HC(O)OCH ₃	23	Jiménez <i>et al.</i> 2016
OH + H ₂ CO	21	Ocaña <i>et al.</i> 2017
CN + CH ₃ CN	23	Sleiman <i>et al.</i> 2016
CN + (CH ₃) _{3-n} NH _n	23	Sleiman <i>et al.</i> 2018a,b
C(³ P, ¹ D) + CH ₃ OH	50	Shannon <i>et al.</i> 2014b

From a theoretical point of view the interest for reactions involving COMs has considerably grown recently and several reactions mentioned in Table 1 have been investigated at interstellar temperatures with a special attention paid on OH + CH₃OH (Shannon *et al.* 2013; Gao *et al.* 2018; Roncero *et al.* 2018; Ocaña *et al.* 2019; Nguyen *et al.* 2019; del Mazo-Sevillano *et al.* 2019) because of its potential importance in the formation of CH₃O (see next section). In the present paper we will review the recent experimental and theoretical works carried out concerning this reaction and will comment about its significance for the chemistry of molecular clouds.

2. The interstellar methoxy radical CH₃O

The discovery of methoxy in the dense interstellar cloud Barnard 1b (T~12K) (Cernicharo *et al.* 2012) was quite challenging for astrochemists because none mechanism included in chemical networks was efficient enough to explain the observed abundance. It was then proposed that the reaction of OH with methanol could be responsible for its production via an hydrogen abstraction from the methyl group of CH₃OH, one of the potential exit routes of the reaction:



Assuming that the branching ratio of reaction 1a is around unity, Balucani *et al.* 2015, proposed a gas phase model in which CH₃O could be the parent of DME CH₃OCH₃ by recombination with a methyl radical. Eventually DME could produce methyl formate by subsequent radical-neutral reactions. As a consequence, CH₃O appeared to be a keystone in the development of molecular complexity and a detailed knowledge of the mechanisms involved in the OH + CH₃OH reaction was clearly desirable.

At first sight however, the OH + CH₃OH reaction was not a good candidate for an abundant formation of methoxy in dense interstellar clouds because of the presence of energy barriers separating products from reactants which cannot be passed over in the low temperature conditions reigning in interstellar molecular clouds. It has been known for a long time that the reaction proceeds via the initial formation of a weakly hydrogen bonded pre-reactive complex PRC* (Galano *et al.* 2002). This can either redissociate back to reactants; relax to its ground state PRC by collisions with the surrounding molecules or pass through the barrier via H-abstraction quantum tunneling. When the surrounding pressure is high enough, it can be assumed that PRC* instantaneously forms PRC in a Boltzmann distribution of energies. This is the so-called High Pressure Limit (HPL) which

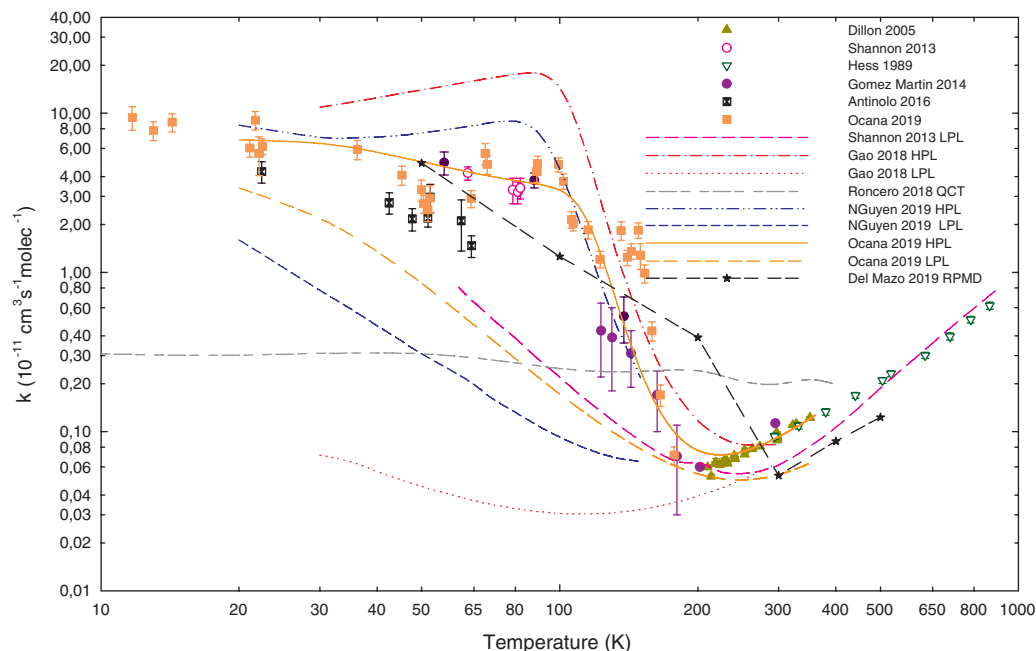


Figure 1. Temperature dependence of the total rate constant $k(T)$ of OH + CH₃OH from experimental and theoretical investigations.

is characterized by a competition between stabilization and tunneling of PRC generally evaluated using several variants of the transition state theory TST. The contribution of the redissociation pathway is then considerably reduced. Opposite, when the surrounding pressure is low enough, PRC* cannot suffer collisions anymore and then competition occurs between redissociation and tunneling at the energy level of PRC*. This is the so-called Low Pressure Limit (LPL). In practice, most of experimental conditions fall in between these two extreme situations and then an energy transfer modeling of PRC* has to be developed making the rate constant of the reaction pressure dependent. Considering the very small densities reigning in dense interstellar clouds ($10^4 - 10^5 \text{ cm}^{-3}$ typically), the LPL regime prevails in these environments.

3. OH + CH₃OH: a decade of experimental and theoretical progress

Figure 1 sums up the various studies concerning the temperature dependence of the total rate constant $k(T)$ making the title reaction one of the more documented radical-neutral reaction. A decade ago however, data were only available above 200 K (Hess & Tully 1989; Dillon *et al.* 2005 for instance). The rate constant exhibited an Arrhenius temperature dependence with a slight curvature below 300 K. Extrapolation down to 10 K resulted in a very small rate constant which could not influence interstellar chemistry. Furthermore, the main product of the reaction was CH₂OH instead of CH₃O.

In 2013 the Leeds group turned upside down the established landscape when they published a series of CRESU measurements at 63 and 80 K (Shannon *et al.* 2013) indicating a tremendous increase of the reaction efficiency, about a factor 70 with respect to the minimum rate constant measured around 200 K. In addition they found no pressure dependence at 80 K and were able to detect the methoxy radical by laser induced fluorescence. To support these results they used the MESMER code to calculate the rate constant for a density of 1000 cm^{-3} and were able to reproduce the experimental $k(T)$ behavior although the absolute value remained 5 times lower than the experiment.

The role of quantum tunneling was decisive in these calculations. Finally, they calculated the branching ratios and found that CH_3O was the only product at $T < 100$ K.

Complementary CRESU measurements were published one year later by the same group in addition to flow tube experiments (Gómez Martín *et al.* 2014) confirming the initial observed behavior. From this, the authors suggested a value of $3 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for the rate constant at 10 K. With this assumption, the $\text{OH} + \text{CH}_3\text{OH}$ reaction was found to be the main source of CH_3O in cold interstellar clouds (Acharyya *et al.* 2015).

Later, the Leeds work was extended down to 22 K in a collaborative investigation between the Rennes and Ciudad Real groups confirming the previous observed trend for the reaction. However, prediction for $k(T=10 \text{ K})$ was lowered by a factor of 3 diminishing the impact of the reaction as a source of CH_3O (Antiñolo *et al.* 2016).

In 2018, an exhaustive theoretical investigation was published by Gao *et al.* in which the authors calculated the rate constants in the HPL and LPL regimes using the Competitive Canonical Unified Statistical theory (CCUS). As they found that the experimental data were bracketed by these two extreme calculations they concluded that the experimental conditions correspond to a pressure dependent regime in contradiction with the Leeds observation at 80 K.

The same year, a quasi-classical trajectory QCT calculation was published by Roncero *et al.* 2018. As the method excludes collisions with a third body, their results can be compared to the LPL data obtained by Gao *et al.* Although they found higher rate constants than Gao *et al.* QCT calculations were not able to reproduce the experimental temperature dependence. The authors argue that the difference with experiment could result from the omission of quantum effects in their calculation (Zero Point Energy + tunneling).

In 2019, the Ciudad Real group did an extensive experimental work in which they evaluated the pressure dependence of the reaction for several temperatures ranging in between 12 and 180 K (Ocaña *et al.* 2019). No pressure dependence was observed below 100 K whereas comparison with the Leeds work suggested some pressure dependence in the range 120 – 150 K. Experiments were completed by theoretical calculations using the Multi-Conformer Canonical TST and RRKM methods for determining the HPL and LPL regimes respectively. This approach was able to reproduce correctly the experimental results in the HPL regime provided that the energy barriers obtained *ab initio* for the transition states were slightly modified and the calculated capture rate constant was scaled to match the experimental values at 20 K. This was in qualitative agreement with the pressure independence found experimentally below 100 K. Interestingly, the LPL calculation converges to the HPL values at the lowest temperatures suggesting that at $T \sim 10$ K, the reaction should be almost pressure independent. This work also confirmed a rate constant of about $10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ at 10 K.

At the same time, another theoretical paper was published in which the authors used a Semi Classical TST model in order to determine the HPL and LPL regimes (Nguyen *et al.* 2019). The significant novelty of this work was the consideration of energy transfer in order to investigate the pressure dependence in between these two extreme limits. The authors were able to match the experimental results assuming a pressure between 200 and 3000 Torr which is however many orders of magnitude higher than the experimental conditions ($\sim 0.1 - 1$ Torr). Similarly to the work by (Ocaña *et al.* 2019), energy barriers were also adjusted with respect to the *ab initio* results. Interestingly, Nguyen *et al.* showed that the rate constant was pressure independent for $P \leq 2$ Torr and $T \leq 100$ K. This indicates that the LPL regime is still valid at significant pressures embedding the experimental conditions. Hence, the pressure independence found experimentally below 100 K could be attributed to a LPL regime as well. Quantitatively speaking however,

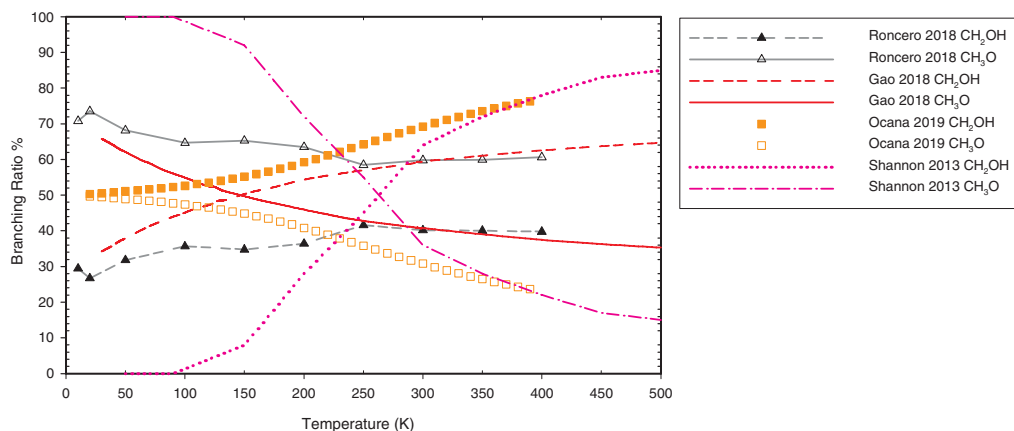


Figure 2. Temperature dependence of the branching ratios leading to the formation of CH₃O and CH₂OH in the LPL regime.

the LPL calculations by Nguyen *et al.* underestimated the experimental values with a significant exception at 10 K for which the agreement was very good.

Finally, it is worth mentioning the very recent calculations from del Mazo-Sevillano *et al.* 2019 which are an extension of the initial work by Roncero *et al.* in 2018. The authors used a combination of the Ring Polymer Molecular Dynamics (RPMD) method and TST technique in order to calculate the temperature evolution of the rate constant considering quantum effects. Their results, again comparable to a LPL situation, led to a satisfactory agreement with experiments. Because the RPMD technique is expected to be more accurate than the TST methodology, the authors suggest that the capture rate constants obtained from TST are underestimated making the HPL calculations fortuitously close to experiments whereas the LPL results remained too low.

The preceding discussion dealt with the total rate constant evolution which is what the present experiments can determine. No quantitative information is presently available experimentally concerning the branching ratios of the two exit H-abstraction channels 1a and 1b. The only evidence for products is the detection of methoxy at 80 K by the Leeds groups as mentioned earlier (Shannon *et al.* 2013). Several of the theoretical investigations however have reported branching ratios calculations. A compilation of these can be seen in Figure 2 for the LPL regime which is the one of interest for the interstellar conditions. LPL calculations lead to a branching ratio for CH₃O in between 50 and 100 % generating a present uncertainty of a factor of 2.

4. Conclusions

The recent experimental and theoretical investigations about the OH + CH₃OH reaction have shed new lights concerning the mechanisms involved. The pressure dependence of the rate constant has been a matter of intense debate which stays still open. However at the very low temperatures of cold interstellar objects (~10 K), the rate constant appears to be almost pressure independent and the last calculations from del Mazo-Sevillano *et al.* suggest that the experimental results are consistent with the LPL regime and therefore representative of the interstellar conditions. Additional effort is still needed in order to fix more precisely the branching ratio leading to the CH₃O formation. From an experimental point of view, several projects are in development in the Rennes group in order to tackle the challenging task of determining branching ratios of radical-neutral reactions. These include association of CRESU reactors with (1) a synchrotron VUV beamline in order to

detect products by threshold photoionization, (2) chirped-pulse microwave spectroscopy (3) frequency combs technique for infrared detection of products.

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