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First evidence of the dramatic enhancement of the reactivity of methyl formate (HC(O)OCH₃) with OH at temperatures of the interstellar medium: A gas-phase kinetic study between 22 K and 64 K

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ABSTRACT. Gas-phase chemistry of neutral-neutral reactions of interest in the interstellar medium (ISM) is poorly-understood. The rate coefficients ($k_{\text{OH}}$) for the majority of the reactions of hydroxyl (OH) radicals with interstellar oxygenated species are unknown at temperatures of the ISM. In this work, we present the first determination of $k_{\text{OH}}$ for HC(O)OCH$_3$ between (22.4±1.4) and (64.2±1.7)K. The CRESU (French acronym for Cinétique de Réaction en Ecoulement Supersonique Uniforme or Reaction Kinetics in a Uniform Supersonic Flow) technique was used to create a chemical reactor with a uniform temperature and gas density and the pulsed laser photolysis/laser induced fluorescence technique was used to generate OH radicals and to monitor their temporal profile. It was observed that $k_{\text{OH}}(T)$ increases one order of magnitude in only ∼40K ($k_{\text{OH}}(T=22K)=$(1.19±0.36)$\times 10^{-10} \text{ cm}^3 \text{s}^{-1}$ and $k_{\text{OH}}(T=64K)=$(1.16±0.12)$\times 10^{-11} \text{ cm}^3 \text{s}^{-1}$), and ~3 orders of magnitude with respect to $k_{\text{OH}}(T=298K)$. This reaction is a very efficient loss route for HC(O)OCH$_3$ in the gas phase and may have a great impact on the interpretation by astrophysical models of the HC(O)OCH$_3$ abundances in cold regions of the ISM.
1 Introduction

Observations of interstellar material started in the last century and nowadays more than 180 species, besides the most abundant H$_2$ and He, are confirmed to be present in the interstellar medium (ISM). Among them, radicals and neutral molecular species containing C, H, and O, such as alcohols, aldehydes, acids and esters, have been detected in dense molecular clouds ($T = 10$-$100$ K) and star-forming regions ($T > 100$ K). For instance, hydroxyl (OH) radicals and methyl formate (HC(O)OCH$_3$) were detected in the ISM molecular clouds.\textsuperscript{1-8}

The observed abundances relative to H$_2$ in hot cores and hot corinos were reported to be $3 \times 10^{-8}$ and $1.4 \times 10^{-8}$ (in Orion), $4 \times 10^{-7}$ (in IRAS 16293-2422) and $7 \times 10^{-7}$ (IRAS 4A). The diverse abundances can be attributed to differences in physical conditions (for instance, the temperature evolution during the warm-up timescale of the object) that affect the chemistry. Recent detections of methyl formate in colder objects, such as protostars Barnard 1b,\textsuperscript{9} in cold environment of IRAS 16293-2422\textsuperscript{10} and prestellar cores\textsuperscript{11} demonstrate that understanding the formation of complex organic molecules (COMs) in these environments is one of the key issues to model properly the observed abundances of these molecules in the ISM.

The formation mechanism of HC(O)OCH$_3$ has been the subject of several studies,\textsuperscript{12-19} but it is not yet well-understood. In hot cores and corinos, it is believed that some organic molecules are formed in grain-surfaces and subsequently injected into the gas phase during the warm-up phase. Once in the gas-phase these molecules are ionized being the precursors of other COMs, such as HC(O)OCH$_3$. Some models exclusively use gas phase reactions, for example, Horn et al.\textsuperscript{12} proposed several formation routes for HC(O)OCH$_3$ via the recombination reaction of a protonated and a neutral species followed
by dissociative recombination with electrons. Nevertheless, this gas-phase chemical model
underpredicts the observed abundances of HC(O)OCH$_3$ in hot cores at $T \sim 100$ K. More
recently, Balucani et al.$^{18}$ proposed a new chemical model for the gas-phase formation of
HC(O)OCH$_3$ in colder environments, based on the fact that ejection of CH$_3$OH takes place
from the outer shell of the cold prestellar core ($T \sim 10$ K) contrary to previous assumptions.
These authors concluded that although the gas-phase formation of methyl formate cannot
be neglected, grain-surface formation is an important formation route for this COM. In gas-
grain models, it is assumed that the formation of HC(O)OCH$_3$ occurs via the reaction of
methoxy (CH$_3$O) and formyl (HCO) at temperatures around 30-40 K, afterwards it is
gradually evaporated into the gas phase.$^{13,14}$ The evidence that the CH$_3$O+HCO reaction
can occur in interstellar granular ices was experimentally proven by Bennett and Kaiser$^{15}$
and Modica and Palumbo.$^{19}$ What is clear is that gas-phase formation of HC(O)OCH$_3$ is
interconnected with grain-surface formation, but what about the removal processes of
HC(O)OCH$_3$ in the gas phase at temperatures of cold objects? Evidently, the gas-phase loss
processes of this COM need to be included as well in chemical models to properly interpret
the observed abundances. Among them, ultraviolet (UV) photodissociation processes and
radical-COM reactions have to be taken into account in the models. UV photodissociation
of methyl formate has been investigated at room temperature (yielding mainly CH$_3$O and
HCO radicals),$^{20-22}$ while the chemical kinetics for the gas-phase reaction of OH radicals
with methyl formate,

$$\text{OH} + \text{HC(O)OCH}_3 \rightarrow \text{Products} \quad k_{\text{OH}},$$  \hspace{1cm} (1)

has been investigated at temperatures between 233 and 1500 K and pressures between 0.4
and 1.63 atm.$^{23-29}$ Up to date no chemical kinetic studies of HC(O)OCH$_3$ have been
reported at lower temperatures. Therefore, the aim of this work is to report for the first time $k_{\text{OH}}$ for reaction (1) between 22 and 64 K, temperatures of interest in the ISM.

2 Experimental

2.1 General Aspects

The CRESU system employed in this work is schematically shown in Figure 1. This setup, which was exhaustively described by Jiménez et al., couples the uniform supersonic gas expansion technique, to achieve the ultra-low temperatures needed for determining $k_{\text{OH}}(T)$ between 22 and 64 K, and the pulsed laser photolysis-laser induced fluorescence (PLP-LIF) kinetic technique.

Ultra-low temperatures are achieved by the isentropic expansion of a gas mixture, consisting in the buffer gas, the OH-precursor (H$_2$O$_2$), and diluted HC(O)OCH$_3$, through a Laval nozzle from a high pressure reservoir ($P_{\text{res}}$) to a vacuum chamber ($P_{\text{cham}}$). In this work, the Laval nozzle described in reference 30 was used for getting all temperatures. This nozzle was initially designed to obtain 22 K in helium (conditions A in Table 1). However, calculations performed with a home-made program, which take into account the existing profile of the divergent-convergent nozzle, indicate that other uniform supersonic flows could be obtained by varying the pressure and temperature conditions as well as the mass flow rates ($F$) for different buffer gases (helium, nitrogen or a mixture of both). The optimal $P_{\text{res}}$ and $P_{\text{cham}}$ and ranges of the calibrated mass flows for the buffer gas ($F_{\text{buffer}}$), the buffer gas through the H$_2$O$_2$ bubbler ($F_{\text{H}_2\text{O}_2}$) and diluted HC(O)OCH$_3$ ($F_{R}$) are summarized in Table 1. In the case of conditions B (see Table 1), the buffer gas is a mixture of He (40%) and N$_2$ (60%) independently introduced in the reservoir. As described elsewhere,
the buffer gas is flowing through a glass bubbler containing a pre-concentrated aqueous solution of H$_2$O$_2$. In case B, N$_2$ was only flowed through the bubbler. Diluted methyl formate was prepared in two 20-L storage bulbs connected in series. Mixing ratios of methyl formate (f) in the 40-L storage bulb ranged from ca. 2×10$^{-3}$ to 8×10$^{-2}$.

The aerodynamic chopper$^{30}$ (rotary disk at 10 Hz) placed at the divergent part of the Laval nozzle was operational under experimental conditions A (hitherto pulsed mode for getting 22 K). The pulsing of the gas was not necessary to achieve higher temperatures (conditions B-D, continuous mode), since the required mass flows and working pressures were accessible with the pumping capacities of our experimental system. In the generated supersonic gas flow the temperature ($T$), the total gas density ($n$), and the velocity are uniform along the flow.

### 2.2. Aerodynamical characterization of the supersonic flows: Pitot tube measurements

The uniformity of these parameters along the axis of the expansion was confirmed by measuring the impact pressure, $P_i$, in the commonly named *Pitot tube* measurements, as a function of the distance from the exit of the nozzle. The Pitot tube used in the continuous mode consisted in a stainless steel tube (5 cm length) with an orifice of 2 mm, which was connected to a 10 or 100 Torr pressure transducer. It was fixed on two manual translational platforms for aligning the Pitot tube with the center of the gas flow. This system was mounted on a motorized long-travel linear translational platform (Standa, 8MT195-740-2.5).
As described in reference 30, the temperature, pressure and gas density of the jet along the uniform supersonic flow were derived from the Mach number, $M$, which is obtained from the average $P_1$ obtained in the optimal length where the flow is uniform:

$$\frac{P_1}{P_{\text{res}}} = \left( \frac{(\gamma + 1)M^2}{(\gamma - 1)M^2 + 2} \right)^{\frac{\gamma}{\gamma - 1}} \left( \frac{\gamma + 1}{2\gamma M^2 - \gamma + 1} \right)^{\frac{1}{\gamma - 1}} \tag{2}$$

The heat capacity ratio $\gamma$ for the buffer gas and $M$ values are shown in Table 2. In particular for the gas mixture He/N$_2$, $\gamma_{\text{mixture}}$ was calculated considering the relationship between the heat capacity of the gas mixture at constant pressure ($C\text{p,mixture}$) and at constant volume ($C\text{v,mixture}$),

$$C\text{p,mixture} = R + C\text{v,mixture}, \tag{3}$$

where $C\text{v,mixture}$ includes the fraction of N$_2$ (60%) and He (40%) in the mixture. Therefore, $\gamma_{\text{mixture}}$ can be expressed in terms of the individual $C\text{v}$ of the gases present in the mixture ($C\text{v,N}_2 = 20.785 \text{ J mol}^{-1} \text{ K}^{-1}$ and $C\text{v,He} = 12.471 \text{ J mol}^{-1} \text{ K}^{-1}$):

$$\gamma_{\text{mixture}} = \frac{R}{0.6 \times C\text{v,N}_2 + 0.4 \times C\text{v,He}} + 1 \tag{4}$$

Temperature and gas densities were then obtained as described in reference 30. As an example, Fig 2 shows the spatial evolution of these two parameters for conditions B (see Figs S1 and S2 of the supporting information for conditions C and D and reference 30 for conditions A). As can be seen in the figures, the temperature and gas density of the jet are uniform for several tens of centimeter from the exit of the nozzle, as well as it prolongs three centimeters inside the divergent part of the nozzle. This length of uniformity is sufficient to carry out the kinetic experiments in a timescale of several hundreds of
microseconds (hydrodynamic time, $t_{\text{hydro}}$, Table 2) and the methyl formate concentrations used (see Table 3).

2.3 PLP-LIF kinetic technique

The conventional PLP-LIF technique has been widely employed in our laboratory for kinetic studies on gas-phase reactions between OH radicals and atmospheric pollutants, as previously described.\textsuperscript{31,32} The OH radical was produced \textit{in situ} by UV photolysis of H$_2$O$_2$ by a KrF excimer laser at 248 nm. The laser fluence measured by a calorimetric disk at the exit of the Laval nozzle was \textit{ca.} 1 mJ/(cm$^2$ pulse) for most of the experiments at 10 Hz. The temporal evolution of OH(X$^2\Pi$) was monitored by LIF at \textit{ca.} 310 nm after excitation of OH at \textit{ca.} 282 nm using a frequency doubled dye laser (Lambda Physik, model Scanmate) pumped by a XeCl excimer laser (Lambda Physik, model LPX105i). The LIF detection arrangement consists of an optical system coupled with a filtered photomultiplier tube, PMT. The band pass filter is centered at 310 nm with a full width at half maximum of 10 nm. The electrical signal from the PMT was transferred to a gated boxcar integration unit and the integrated signal was recorded and processed into a computer by a home-made LabView program.

OH radicals were lost mainly by reaction with methyl formate and at a lesser extent by reaction with H$_2$O$_2$ ($k_{\text{prec}}$) and other processes such as diffusion of OH radicals out of the detection zone and/or reaction with impurities, if present in the sample. As mentioned in section 2.2, the timescale of the kinetic experiment was restricted by the uniformity of the supersonic flow. For that reason, at all temperatures the maximum reaction time is the
hydrodynamic time, mentioned in Table 2. The reaction time during the kinetic measurements was varied by changing the delay between the photolysis and the probe lasers from ca. 20-40 µs before the trigger of the photolysis laser (to record the background signal) to the hydrodynamic time.

2.4 Chemicals

He (99.999%, Praxair) and N\(_2\) (99.999%, Praxair) were used as supplied. Liquid sample of anhydrous HC(O)OCH\(_3\) (99%, Sigma-Aldrich) was placed in a flask (\(V = 250\) mL) degassed by repeated freeze-pump-thaw cycles prior to its use. During the preparation of diluted methyl formate in the buffer gas, the flask containing the liquid was introduced in a beaker with water at room temperature to thermalize the sample, since there is a small gas expansion and, consequently, temperature and vapor pressure of the methyl formate decrease. Aqueous solution of H\(_2\)O\(_2\) (Sharlab, initially at 50% w/v) was pre-concentrated as described earlier.\(^{31,32}\)

3 Results and Discussion

3.1. Determination of \(k_{\text{OH}}(T)\)

The kinetic study of reaction (1) was performed under pseudo-first order conditions ([OH]\(_0\ll[\text{HC(O)OCH}_3\]) and [H\(_2\)O\(_2\)]. [HC(O)OCH\(_3\)] concentration was calculated from the dilution factors, the mass flow rates, and \(T\) and \(P\) of the jet. Concentration ranges used in the kinetic analysis are shown in Table 3. In order to check that the pseudo-first order conditions were accomplished, the gas-phase concentration of H\(_2\)O\(_2\) in the jet was optically measured before entering the reservoir (at room temperature) by UV spectroscopy at 254
nm using a gas cell with a path length of 108 cm. After correction of temperature and pressure (for conditions D), \([\text{H}_2\text{O}_2]\) in the jet was found to be lower than \(10^{13} \text{ cm}^{-3}\) in this case. Accurate calculation of \([\text{OH}]_0\) would require the knowledge of absorption cross section of \(\text{H}_2\text{O}_2\) at 248 nm and the OH quantum yield at lower temperatures than 298 K. Nicovich and Wine\(^{33}\) measured the temperature dependence of \(\sigma_\lambda\) for \(230 \text{ nm} \leq \lambda \leq 295 \text{ nm}\) between 285 and 381 K. No appreciable change was observed in \(\sigma_\lambda\) in this wavelength range. In any case, at the photolysis laser fluence used and considering the absorption cross section of \(\text{H}_2\text{O}_2\) and quantum yield of OH at room temperature,\(^{34}\) the initial OH concentration between 22 K and 64 K is expected to be several orders of magnitude lower (below \(10^{10} \text{ cm}^{-3}\)) than that of its precursor. Consequently, the \textit{pseudo}-first order conditions are achieved at all reagent concentrations.

In the absence of OH-precursor, Le Calvé \textit{et al.}\(^{26}\) detected a fluorescence emission at 310 nm attributed to \(\text{CH}_3\text{O}\) radicals formed in the photolysis of methyl formate, \((1.94-6.85) \times 10^{15} \text{ cm}^{-3}\), at 248 nm. In the present work, nonetheless, no emission was observed in the photolysis of methyl formate at 248 nm in the absence of \(\text{H}_2\text{O}_2\) at the concentrations and laser fluences employed. Therefore, the recorded LIF temporal profiles correspond exclusively to OH radicals. \textbf{Fig 3} shows an example of the temporal evolution of OH radicals in the presence of methyl formate recorded at 43 K. The temporal profiles of the OH LIF signal \((I_{\text{LIF}})\) were analyzed after 20-40 \(\mu\)s depending on the methyl formate concentration, because some rotational relaxation occurs at shorter times. At all temperatures of the jet, \(I_{\text{LIF}}\) did not fully decay in the available timescale at the methyl formate concentrations, which had to be low enough to avoid secondary chemistry (as discussed below).
Under these conditions and after rotational relaxation of OH, the non-linear least square fit of the LIF data to a single exponential function (solid line in Fig 3) yields the pseudo-first order rate coefficient, $k'$, for a fixed concentration of methyl formate (and H$_2$O$_2$):

$$k' = k_{\text{OH}}(T)[\text{HC(O)OCH}_3] + k_0$$  \hspace{1cm} (5)

where $k_0$ ($= k_{\text{prec}}(T)[\text{H}_2\text{O}_2] + k_{\text{other losses}}$) is the pseudo-first order coefficient obtained in the absence of HC(O)OCH$_3$. During a kinetic experiment at a single temperature, [H$_2$O$_2$] was kept constant. Averaged $k_0$ (in s$^{-1}$) were 6400 at 22 K, 3700 at 43 K, 2100 at 52 K and 5100 at 64 K. Individual $k_{\text{OH}}(T)$ were obtained from the slope of the plots of the pseudo-first order rate coefficients $k'$ corrected by $k_0$ against the HC(O)OCH$_3$ concentrations.

$$k' - k_0 = k_{\text{OH}}(T)[\text{HC(O)OCH}_3]$$  \hspace{1cm} (6)

All obtained $k'$-$k_0$ are plotted as a function of reactant concentration in Fig 4 for all experiments carried out. As it can be seen in Fig 4.a, at 22 K a curvature in the plot of $k'$-$k_0$ versus [HC(O)OCH$_3$] was observed above $3 \times 10^{13}$ cm$^{-3}$, indicating that an additional loss of methyl formate is occurring by complexing formation in the ultracold jet ($T$=22 K). This effect was also observed in the reaction of OH with 1-butene at 22 K. For that reason the kinetic analysis was constrained to the range of [HC(O)OCH$_3$] where pseudo-first order plots were linear. As can be seen in Table 3 and Fig 4, higher concentrations of HC(O)OCH$_3$ could be accessible at higher temperatures, because the formation of aggregates is kinetically less efficient at the total gas density of these experiments with respect to 22 K.

### 3.2. Temperature Dependence of $k_{\text{OH}}(T)$: Enhancement at ultra-low temperatures
$k_{\text{OH}}(T)$ values obtained are listed in Table 3 and depicted in Fig 5. As it can be seen, the reactivity of HC(O)OCH$_3$ toward OH radicals is high in the investigated temperature range, decreasing rapidly from 22 to 64 K. In Table 3, the enhancement factor relative to $k_{\text{OH}}(64\text{K})$ is also shown for all temperatures. The observed enhancement of $k_{\text{OH}}(T)$ over 40 K in the $T$-range of interest in the ISM is of one order of magnitude. The enhancement factor is ca. 4 and 2 at 43 and 52 K, respectively.

The observed temperature dependence of $k_{\text{OH}}(T)$ between 22 and 64 K was first fitted to the following expression commonly used in kinetic databases employed in astrophysical models:\textsuperscript{35}

$$k_{\text{OH}}(T) = \alpha \left( T / 300 \text{ K} \right)^{\beta} \exp(-\gamma / T)$$ \hspace{1cm} (7)

The fit to this three-parameter expression yielded a $\gamma \sim 0$ K. Therefore, we deliberately fixed this parameter to 0 K without affecting significantly the accuracy of the fit. As $\beta<0$ (see Fig 5), extrapolation of Eq.(7) to temperatures close to absolute zero ($T<22$ K) provides however unrealistic results ($T \rightarrow 0$ K, $k_{\text{OH}}(T) \rightarrow \infty$). Interestingly, a single exponential expression of the form,

$$k_{\text{OH}}(T) = a \exp(-b \times T),$$ \hspace{1cm} (8)

describes perfectly the observed $T$-dependence of $k_{\text{OH}}(T)$ in the investigated range. The resulting parameters $a$ and $b$ are given in Fig 5. Note that even though Eq.(8) has no physical meaning, it predicts a reasonable $k_{\text{OH}}$ at 10 K ($2.38 \times 10^{-10}$ cm$^3$ s$^{-1}$) and at 0 K ($3.84 \times 10^{-10}$ cm$^3$ s$^{-1}$). Of course, the “real” kinetic behavior may be different as that predicted, hence Eq.(8) should be exclusively used for the temperature range 22-64 K.

As shown in Table 4 and Fig 6, the trend in the temperature dependence of $k_{\text{OH}}(T)$ is noticeably different at $T<64$ K (of interest in the ISM, this work), between 233 and 372 K.
(of interest in terrestrial atmosphere)\textsuperscript{23-27,29} and at higher temperatures (of interest in combustion chemistry)\textsuperscript{27,28} At room temperature, Wallington \textit{et al.}\textsuperscript{23}, Good \textit{et al.}\textsuperscript{24} and Szilagyi \textit{et al.}\textsuperscript{25} reported experimental rate coefficients $k_{\text{OH}}(T)$ in quite good agreement with each other. The typical measured value was about $2 \times 10^{-13}$ cm$^3$ s$^{-1}$. Le Calvé \textit{et al.}\textsuperscript{26} extended the kinetic study of reaction (1) to temperatures between 233 and 372 K. These authors observed a small positive temperature dependence with an activation energy of \textit{ca.} 1 kcal/mol. At temperatures of interest in combustion chemistry, Lam \textit{et al.}\textsuperscript{27} experimentally reported a much stronger temperature dependence with activation energy of 4 kcal/mol between 880 and 1337 K.

From a theoretical point of view, a few works can be found in the literature. In 1999 Good \textit{et al.}\textsuperscript{24} used \textit{ab initio} molecular orbital theory to calculate the rate coefficient at 298 K obtaining a value of $1.88 \times 10^{-13}$ cm$^3$ s$^{-1}$, in excellent agreement with their experimental contribution and other studies. The rate coefficient was calculated by transition state theory (TST) taking into account the Wigner correction accounting for the effect of tunneling. More recently, Tan \textit{et al.}\textsuperscript{28} performed \textit{ab initio} calculations in the temperature range 300-1500 K, and found that $k_{\text{OH}}(300K) \sim 8 \times 10^{-15}$ cm$^3$ s$^{-1}$ which is lower, by more than one order of magnitude, than the experimental ones. TST in conjunction with the CANTHERM code was used by Tan \textit{et al.}\textsuperscript{28} to calculate these rate coefficients and the Eckart correction was applied to take into account tunneling. A third study was provided by Elm \textit{et al.}\textsuperscript{29} The originality of their work was to calculate the rate coefficient at 298 K and 1 atm for several functionals and tunneling corrections using the conventional TST. They concluded that BH&HLYP and MP2 functionals were those leading to the best agreement with experiments, provided that the tunneling Bell correction was used. Interestingly, the rate
coefficient was increased by a factor of 36 (BH&HLYP) or 90 (MP2) when the Bell correction was applied to their UCCSD(T)-F12a single point corrected \(k_{OH}(298K)\) indicating the very large effect of tunneling in this reaction.

To our knowledge, no attempt has been undertaken to determine rate coefficients at sub-ambient temperatures using these theoretical methods. As it can be seen in Fig 6, an increase of roughly three orders of magnitude for \(k_{OH}(T)\) is observed between 298 K and 22 K, whereas the rate coefficient shows a classical Arrhenius increase at higher temperatures. This kind of behavior has been seen for the first time only very recently for other oxygenated compounds reacting with OH. This spectacular change in \(k_{OH}\) could be explained by a change in the mechanism driving the dynamics of the reaction comparing to the suprathermal domain.

3.3. Reaction mechanisms and products

The reaction pathways of the \(\text{OH} + \text{CH}_3\text{C(O)OH}\) reaction have been investigated by Good et al. and more extensively by Tan et al.. In the latter study, the authors found that the reaction proceeds through H abstraction at either the methyl group or the formyl group of methyl formate, leading to the exothermic formation of \(\text{CH}_2\text{C(O)OH} + \text{H}_2\text{O}\) or \(\text{CH}_3\text{C(O)O} + \text{H}_2\text{O}\), respectively. Four reaction pathways were identified, all starting with the reversible formation of a weakly bound pre-reactive complex followed by an irreversible reaction through a transition state to the above mentioned products. As two pre-reactive complexes have been found to stand in a very shallow well (~1 kcal/mol), only those channels passing through the deeper wells (3.7 and 3.4 kcal/mol, respectively) have been considered by the authors. The barrier heights for the two corresponding transition
states were 3.5 and 4.0 kcal/mol respectively. This situation is qualitatively similar to that observed for the reaction of OH with methanol\textsuperscript{37,39}, acetone\textsuperscript{36,38} and dimethyl ether\textsuperscript{36,38} and can qualitatively explain our observations. The pre-reactive complexes are expected to be short-lived at "high" temperatures with the propensity to break back to the reactants, whereas the activation barrier to the transition state leads to a standard Arrhenius behavior. At lower temperatures, the pre-reactive complex lifetime should raise giving a chance to the rate coefficient to increase significantly either by adduct stabilization (three body process) or tunneling through products (binary process). Although the present experimental study cannot discriminate from these two options, the theoretical work carried out by Elm \textit{et al.}\textsuperscript{29} showed that tunneling has a major contribution, at least at 298 K. This should be even stronger at lower temperatures. Note that terms such as "high" and "low" are presently quite vague, because there is no sufficient data available to identify the temperature at which the rate coefficient would reach its minimum value. Further experimental and theoretical works are evidently needed to make these aspects clearer.

3.4. Branching ratios

Another aspect to consider is the potential organic radical formation in reaction (1). Quantitative information concerning the products of reaction (1) cannot be derived from the present experiments, nevertheless some comments are worthwhile. As mentioned earlier, in the titled reaction, hydrogen atom abstraction by OH radicals can occur at either the formyl group (channel 1a) or the methyl group (channel 1b):

\[
\text{OH} + \text{HC(O)OCH}_3 \rightarrow \text{C(O)OCH}_3 + \text{H}_2\text{O} \quad (1a)
\]
\[
\rightarrow \text{HC(O)OCH}_2 + \text{H}_2\text{O} \quad (1b)
\]
At 298 K, Le Calvé et al.\textsuperscript{24} predicted, based on structure-activity (SAR) calculations that both channels accounted for ca. 50% of the overall rate coefficient $k_{\text{OH}}$. From \textit{ab initio} calculations, the predicted branching ratio $k_{1a}/k_{1b}$ at room temperature greatly differs. Good et al.\textsuperscript{25} reported that that formation of C(O)OCH\textsubscript{3} radicals (channel 1a) was the major reaction pathway, accounting for 86%, while Tan et al.\textsuperscript{28} predicted that formation of HC(O)OCH\textsubscript{2} radicals (channel 1b) was the major reaction pathway, accounting for 66% of $k_{\text{OH}}$. At higher temperatures (e.g. 1168 K), Lam et al.\textsuperscript{27} estimated that channel (1b) is the main reaction pathway accounting for 68% of overall $k_{\text{OH}}$, which is lower than that derived from \textit{ab initio} calculations by Tan et al.\textsuperscript{28} (ca. 54% for channel 1b). In light of these discrepant results and given that the formation of C(O)OCH\textsubscript{3} and HC(O)OCH\textsubscript{2} radicals is not quantitatively known, we cannot assert which channel could become more important at lower temperatures than 298 K. However, by comparison with the reaction of OH with CH\textsubscript{3}OH, it could be expected a change in the yield of the reaction products at low temperatures with respect to that found at room temperature.\textsuperscript{37} According to master equation calculations carried out by Shannon et al., the H-atom abstraction by OH radicals seems to exclusively occur at low temperatures from the –OH group of methanol.\textsuperscript{37} These calculations show that the branching ratio for the CH\textsubscript{3}O + H\textsubscript{2}O channel reaches unity at temperatures lower than 70 K. In contrast, at room temperature the main reaction product is CH\textsubscript{2}OH radical formed through the H-abstraction from methyl group of methanol.\textsuperscript{41} Further mechanistic studies on reaction (1), especially at low temperatures are indispensable to check if the C(O)OCH\textsubscript{3} radical can be the main reaction product at temperatures of the ISM.
4. Conclusions and astrophysical impact

The present work constitutes the first determination of the rate coefficients for the gas-phase reaction of methyl formate and OH radicals at ultra-low temperatures. Our results show that, at extremely low temperatures, the investigated reaction (1) is a very efficient loss route for HC(O)OCH₃ in the gas phase, up to three orders of magnitude faster than at room temperature. Acharyya et al.⁴² have recently evidenced the importance of determining gas-phase rate coefficients at temperatures found in ISM molecular clouds (close to 10 K) for the reaction of OH with methanol. The acceleration of $k_{\text{OH}}$ for this reaction has a marked influence on the modeled abundances of CH₃O radicals. For that reason, the inclusion of our results on the OH+methyl formate in astrochemical models may have a great impact and would help to improve/shed light on the interpretation of the detected abundances of methyl formate in the various environments of the ISM. These measurements can also stimulate attempts to detect the radicals issued from the studied reaction, which have not been looked for until now.

The temperature dependence of reaction (1) has been found to be similar to that observed for other oxygenated species reacting with OH⁵⁵-³⁹. With the exception of the reaction of OH with methanol, Shannon et al.⁵⁷ and Caravan et al.⁴⁹ reported that a pressure dependence of $k_{\text{OH}}(T)$ was observed at gas densities between $3.2 \times 10^{16}$ and $2.6 \times 10^{17}$ cm⁻³ in the temperature range ca. 88 and 140 K⁵⁷,⁴⁹. Despite the present work cannot provide any evidence of a pressure dependence of the rate coefficient $k_{\text{OH}}$, this will be explored in the near future with specific Laval nozzles, operating at different gas densities for a same temperature.
Further CRESU experiments are also needed at different temperatures to have a complete picture of the kinetic behavior of reaction (1) at sub-ambient temperatures. For this purpose, new Laval nozzles will be constructed in our laboratory to probe temperatures below 20 K and above 64 K.
Acknowledgments

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References


Fig 1. Schematics of the experimental system employed: CRESU apparatus coupled to PLP-LIF.
Fig 2. Spatial profiles of the temperature and total gas density of the jet for experimental conditions B. Uncertainty is ±σ.
Fig 3. Example of a temporal profile of the LIF signal from OH radicals recorded at $T = 43$ K in the presence of methyl formate ($1.86 \times 10^{13}$ cm$^{-3}$). The fit started at 20 µs to ensure fully rotational relaxation of OH.
Fig 4. Plots of corrected pseudo-first order rate coefficient versus methyl formate concentration.
Fig 5. Temperature dependence of $k_{\text{OH}}(T)$ for the reaction of OH with methyl formate between 22 and 64 K.
**Fig 6.** Temperature dependence of $k_{\text{OH}}(T)$ for the investigated reaction (1) between 22 and 1344 K.
Tables

Table 1. Summary of the experimental conditions employed in this work ($T_{\text{res}} = 297\pm1$ K).

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Gas Flow</th>
<th>Buffer Gas (%)</th>
<th>$F_{\text{He}}$/slpm</th>
<th>$F_{\text{N}_2}$/slpm</th>
<th>$F_{\text{buffer}}$/slpm</th>
<th>$F_{\text{H}_2\text{O}_2}$/scm</th>
<th>$F_{R}$/sccm</th>
<th>$f \times 10^3$</th>
<th>$P_{\text{res}}$/mbar</th>
<th>$P_{\text{cham}}$/mbar</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pulsed</td>
<td>He (100%)</td>
<td>8.4</td>
<td>0</td>
<td>8.4</td>
<td>95-190</td>
<td>48-592</td>
<td>1.9-12</td>
<td>337.0</td>
<td>0.621</td>
</tr>
<tr>
<td>B</td>
<td>Continuous</td>
<td>N$_2$ (60%)</td>
<td>6.0</td>
<td>9.0</td>
<td>15.0</td>
<td>190</td>
<td>45-550</td>
<td>37-77</td>
<td>127.1</td>
<td>0.296</td>
</tr>
<tr>
<td>C</td>
<td>Continuous</td>
<td>N$_2$ (100%)</td>
<td>0</td>
<td>12.6</td>
<td>12.6</td>
<td>190</td>
<td>47-562</td>
<td>50-55</td>
<td>136.2</td>
<td>0.279</td>
</tr>
<tr>
<td>D</td>
<td>Continuous</td>
<td>N$_2$ (100%)</td>
<td>0</td>
<td>4.4</td>
<td>4.4</td>
<td>47</td>
<td>48-573</td>
<td>19-38</td>
<td>41.67</td>
<td>0.183</td>
</tr>
</tbody>
</table>

* Flow of buffer gas through the bubbler containing the aqueous solution of OH precursor; $F_R$ is the flow rate of the diluted methyl formate through the reservoir; $f$ is the dilution factor of the methyl formate in the storage bulb.
Table 2. Characteristics of the gas flows: average impact pressure ($P_i$), heat capacity ratio ($\gamma$), Mach number ($M$), temperature of the jet ($T$), hydrodynamic time ($t_{\text{hydro}}$) and the length of the flow uniformity ($d$).

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$P_i$/mbar</th>
<th>$\gamma$</th>
<th>$M$</th>
<th>$T$/K</th>
<th>$t_{\text{hydro}}$/µs</th>
<th>$d$/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>29.1±2.6</td>
<td>1.6667</td>
<td>6.1±0.2</td>
<td>22.4 ±1.4</td>
<td>244</td>
<td>40</td>
</tr>
<tr>
<td>B</td>
<td>10.5±0.6</td>
<td>1.4762</td>
<td>5.0±0.1</td>
<td>42.5±1.3</td>
<td>414</td>
<td>32</td>
</tr>
<tr>
<td>C</td>
<td>9.3±0.7</td>
<td>1.4000</td>
<td>4.9±0.1</td>
<td>51.6±1.7</td>
<td>777</td>
<td>52</td>
</tr>
<tr>
<td>D</td>
<td>4.7±0.3</td>
<td>1.4000</td>
<td>4.2±0.1</td>
<td>64.2±1.7</td>
<td>202</td>
<td>11</td>
</tr>
</tbody>
</table>
Table 3. Rate coefficients for the gas-phase reaction of OH with methyl formate between 22 and 64 K and enhancement factors with respect to $k_{\text{OH}}$ at 64 K.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$T$ / K</th>
<th>$n$ / $10^{16}$ cm$^{-3}$</th>
<th>[HC(O)OCH$_3$] / $10^{13}$ cm$^{-3}$</th>
<th>$k_{\text{OH}}(T)^a / 10^{-11}$ cm$^3$ s$^{-1}$</th>
<th>$k_{\text{OH}}(T) / k_{\text{OH}}(64\text{K})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>22.4 ±1.4</td>
<td>17.2±1.6</td>
<td>0.20-3.00</td>
<td>11.9±0.36</td>
<td>10.3</td>
</tr>
<tr>
<td>B</td>
<td>42.5±1.3</td>
<td>5.22±0.33</td>
<td>0.62-9.20</td>
<td>4.39±0.52</td>
<td>3.8</td>
</tr>
<tr>
<td>C</td>
<td>51.6±1.7</td>
<td>4.17±0.35</td>
<td>0.77-9.20</td>
<td>2.51±0.30</td>
<td>2.2</td>
</tr>
<tr>
<td>D</td>
<td>64.2±1.7</td>
<td>2.24±0.15</td>
<td>0.54-9.70</td>
<td>1.16±0.12</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ Uncertainties are ±2σ, statistical and 10% due to systematic errors
Table 4. Literature values of the Arrhenius parameters, $k_{OH}(T) = A \exp(-E_a/RT)$, and experimental room temperature rate coefficient for the titled reaction.

<table>
<thead>
<tr>
<th>$T/\text{K}$</th>
<th>$k_{OH}(298\text{K})/10^{-13}\text{cm}^3\text{s}^{-1}$</th>
<th>$A/10^{-12}\text{cm}^3\text{s}^{-1}$</th>
<th>$(E_a/R)/\text{K}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>2.27±0.34</td>
<td></td>
<td></td>
<td>Wallington et al. $^{23}$</td>
</tr>
<tr>
<td>298</td>
<td>1.77±0.28</td>
<td></td>
<td></td>
<td>Good et al. $^{24}$</td>
</tr>
<tr>
<td>298</td>
<td>1.83±0.33</td>
<td></td>
<td></td>
<td>Szilagyi et al. $^{25}$</td>
</tr>
<tr>
<td>233 - 372</td>
<td>1.84</td>
<td>0.854±0.198</td>
<td>461±70</td>
<td>Le Calvé et al. $^{26}$</td>
</tr>
<tr>
<td>880-1344</td>
<td>-</td>
<td>42.5</td>
<td>2026</td>
<td>Lam et al. $^{27}$</td>
</tr>
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