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Gas-phase kinetics of CH₃CHO with OH radicals between 11.7 and 177.5 K

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Abstract

Gas-phase reactions in the interstellar medium (ISM) are a source of molecules in this environment. The knowledge of the rate coefficient of neutral-neutral reactions as a function of temperature, $k(T)$, is essential to improve the astrochemical models. In this work, we have experimentally measured $k(T)$ for the reaction between the OH radical and acetaldehyde, both present in many sources of ISM. Laser techniques coupled to a CRESU system were used to perform kinetic measurements. The obtained modified Arrhenius equation is $k(T=11.7 - 177.5 \text{ K}) = (1.2 \pm 0.2) \times 10^{-11} (T/300 \text{ K})^{-(1.8 \pm 0.1)} \exp(-28.7 \pm 2.5)/T \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. $k(T)$ of the title reaction has been measured for the first time below 60 K. No pressure dependence of $k(T)$ was observed at *ca.* 21, 50, 64 and 106 K. Finally, a pure gas-phase model indicates that the title reaction could become the main CH₃CO formation pathway in dark molecular clouds, assuming CH₃CO is the main reaction product at 10 K.

Introduction

Chemistry in space occurs mostly wherever gas is dense (10^4 cm^{-3}) and cool enough (10-20 K) to form chemical bonds, producing a wide variety of molecules, as well as in other warmer environments (50-200 K). These are particularly common in the clouds of the interstellar medium (ISM) that provide the raw material for star and planet formation. Currently, around 200 different molecules have been detected in the ISM, being about one third the so-called complex organic molecules (COMs) that contain six or more atoms.¹

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Conflicts of interest

There are no conflicts to declare.

A relatively abundant molecule in these cold and dense environments is the hydroxyl radical (OH), which is a key intermediate in many reactive processes there.^{2–5} Its first astrophysical detection was reported in 1963 by Weinreb *et al.*⁶ in Cassiopeia A, with a column density of the order of 10^{14} cm^{-2} , giving a typical abundance of 10^{-7} relative to H. Among the interstellar COMs, acetaldehyde (CH_3CHO) has been detected in many astronomical objects, such as in Taurus molecular cloud 1,^{7, 8} Class I hot corino of SVS13-A protostar,⁹ HH212 hot corino,¹⁰ L134N cold dust cloud,⁸ Sagittarius B2^{11–15} as well as in other regions of star formation.^{16–18} Table 1 summarizes the observed abundances of CH_3CHO in those astronomical sources. The origin of CH_3CHO in the ISM is not well understood yet and several mechanisms have been proposed to explain its presence in the ISM.^{18, 19} Charnley¹⁸ evaluated the possible pathways reactions to produce CH_3CHO in star-forming regions, including gas-phase reactions with ion-neutral and neutral-neutral species, and grain-surface reactions, notably reducing and oxidizing reactions. He concluded that grain-surface reactions can be responsible for the production of CH_3CHO and $\text{C}_2\text{H}_4\text{O}$ isomers in hot molecular cores, rather than gas-phase reactions. Rawlings *et al.*,²⁰ based on the idea of explosive sublimation of ice mantles, proposed the three-body reaction of CH_3 , HCO and H_2O to yield CH_3CHO , in environments such as dark interstellar clouds.

Knowledge of the gas-phase reactivity between CH_3CHO and OH is needed at typical temperatures of the ISM in order to better understand the role of this reaction in the formation of other COMs. For instance, the CH_3CO radical is a potential product of the title reaction via the H-abstraction by OH radicals from the aldehydic group. Although not yet detected in the ISM, Das *et al.*²⁶ proposed that CH_3CO can be involved in the formation of methyl acetate ($\text{CH}_3\text{OC(O)CH}_3$) in the ISM. Other authors proposed that CH_3CHO and CH_3CO can be involved in grain surface,^{27, 28} bimolecular,^{29–31} and even termolecular³⁰ processes at temperatures between 10 and 200 K in the ISM or in planetary atmospheres.

The kinetics of the reaction of OH with CH_3CHO has been the subject of several studies at room temperature as well as at atmospheric and combustion temperatures.^{32–50} This reaction may proceed by the following thermodynamically accessible channels:

Theoretical calculations and experimental determinations suggest that H-abstraction from the aldehydic group (R1) is the main pathway of this reaction at room temperature.^{39, 51–61} and higher temperatures.⁴² At room temperature, Butkovskaya *et al.*⁵⁴ determined the branching ratio for reaction (R2) to be *ca.* 0.05, supporting that the main pathway is reaction (R1).

As proposed by computational calculations,^{41, 59} the title reaction occurs mainly through a pre-reactive complex with a lower energy relative to the reactants, followed by a transition state and finally forming $\text{CH}_3\text{CO} + \text{H}_2\text{O}$. Recently, Howes *et al.*⁵¹ reported that CH_3CO is formed chemically activated in reaction (R1) and measured the yield of formation of CH_3

radicals from the decomposition of excited CH_3CO at 298 K. The CH_3 yield was pressure dependence and the zero pressure yield ranged from 12 to 20%.

Only one investigation was carried out at temperatures below 200 K. Vöhringer-Martinez *et al.*⁴¹ reported the rate coefficient for the gas-phase $\text{OH}+\text{CH}_3\text{CHO}$ reaction, $k(T)$, between 60 and 118 K. Interestingly, these authors showed that addition of water vapour in their supersonic reactor induced a catalytic effect on the OH removal. Here, we present a comprehensive experimental study on the determination of $k(T)$ for the $\text{OH}+\text{CH}_3\text{CHO}$ reaction by extending the temperature range between 11.7 and 177.5 K. Measurements of $k(T)$ were made possible by combining a pulsed/continuous CRESU (French acronym for *Reaction Kinetics in a Uniform Supersonic Flow*) reactor with laser techniques. To study the potential pressure dependence of $k(T)$, further kinetic measurements were performed at selected temperatures (*ca.* 21, 50, 64 and 106 K) covering the gas density (n) range of $(1.50 - 19.5) \times 10^{16} \text{ cm}^{-3}$, which corresponds to a pressure (P) range of (0.11 - 1.42) mbar.

A comparison with previous results is included together with a discussion on the observed reactivity trend at very low temperatures. Finally, a pure gas-phase astrochemical model has been developed to evaluate the importance of the present results on the potential formation of CH_3CO radicals in dark molecular clouds.

Experimental Procedures

CRESU technique and experimental set-up

Many kinetic studies of gas-phase OH-reactions have been conducted at interstellar temperatures by our research group, *e.g.* with acetone,⁶² methanol,^{63, 64} ethanol,⁶⁵ formaldehyde,⁶⁶ or methyl formate.⁶⁷ These studies and the present work employed a pulsed and continuous CRESU apparatus, described in detail elsewhere.^{62–69} Hence, only a brief description is given below.

The CRESU technique is based on the isentropic supersonic expansion of a gas mixture (mainly formed by an inert gas) from a relative high-pressure *reservoir* (or pre-expansion chamber) to a relative low-pressure chamber through a Laval nozzle. In this work, a set of 7 Laval nozzles were used to cover the whole temperature range (11.7–177.5 K). The aerodynamic characterization of most of the nozzles was reported in previous works.^{62–69} In the present study, the uniformity of the jet in temperature, pressure and density was checked for 5 Laval nozzles (He15K, He23K-LP, He23K-IP, Ar50K and Ar100K that yield average jet temperatures of (14.6 ± 1.0) K, (18.6 ± 0.6) K, (26.9 ± 1.1) K, (76.0 ± 0.8) K and (135.0 ± 0.8) K respectively. During expansion, an isentropic core is generated in the jet with temperature and P , relatively constant throughout several tens of centimetres from the nozzle exit.⁶⁹ This gas mixture is pulsed by an aerodynamic chopper (*i.e.*, a rotary disk) which is placed in the divergent part of the Laval nozzle.⁶⁸ At temperatures higher than 13.0 K, a disk with two symmetrical apertures, which pulses the jet at 10 Hz, is employed. However, for the experiments performed at 11.7 K and 13.0 K another rotary disk with one ovoid aperture is used, pulsing the gas at 5 Hz.

The total flow (F_{total}) of the gas mixture, introduced in the pre-expansion chamber, consists in a main flow of an inert gas (He, Ar or N_2) or a binary mixture of N_2 and Ar or He (F_{buffer}), a flow through a bubbler containing the photolytic OH-precursor, H_2O_2 ($F_{\text{H}_2\text{O}_2}$), and a small flow of a diluted CH_3CHO in the buffer gas ($F_{\text{CH}_3\text{CHO}}$). Gaseous H_2O_2 was introduced into the *reservoir* by flowing a small portion of the bath gas through a mass flow controller (MFC) before entering a bubbler which contains a pre-concentrated aqueous solution of H_2O_2 . The temperature of the bubbler was kept constant by immersing it in a room temperature water bath to avoid vapour pressure variations during the kinetic experiments. It was also covered with a black cloth to avoid its photodissociation by room light. The dilution factor of acetaldehyde ($f_{\text{CH}_3\text{CHO}}$) ranged from 0.001 to 0.051 as shown in Table S1 in the ESI†. All gas flows were controlled by a MFC that was regularly calibrated for the buffer gas employed (Sierra Instruments, Inc., model Smart-Trak, Smart-Trak 2, Micro-Trak 101 and Smart-Trak 100). In Table S1 in the ESI†, the mass flow ranges for each gas mixture are listed together with the rest of experimental conditions employed: T , n , buffer gas (or a mixture of buffer gases), $f_{\text{CH}_3\text{CHO}}$, different flows rates and $[\text{CH}_3\text{CHO}]$ range.

Procedure and kinetic analysis

The OH radicals were generated *in situ* in the jet by pulsed laser photolysis of gaseous H_2O_2 at 248 nm, using a KrF excimer laser (Coherent, model ExciStar XS 200). The photolysis laser fluence ranged from 0.5 to 2.6 $\text{mJ pulse}^{-1} \text{cm}^{-2}$ at 10 Hz, depending on the nozzle used. The OH radicals formed in the electronic ground state ($\text{OH}(\text{X}^2\Pi)$) were, then, excited at *ca.* 282 nm. This radiation was achieved by a KDP crystal in a doubling unit of a dye laser (Lambda Physik, model Scanmate; and LiopTec, model LiopStar), pumped by the second harmonic of a Nd:YAG laser (Continuum, model Surelite; and InnoLas, model SpitLight 1200). The loss of $\text{OH}(\text{X}^2\Pi)$ by reaction with CH_3CHO (R3), H_2O_2 (R4) or other loss processes (R5) was monitored as a function of the reaction time by laser induced fluorescence (LIF) at *ca.* 310 nm.

The LIF signal was collected by a photomultiplier tube (Electron Tube, model 9813B) with a bandpass filter centred at 310 nm (Andover Co., model 310FS10-25) and processed by a gated boxcar integration unit (Stanford Research System, model SRS250). The integrated signal was treated and recorded by a homemade LabView program on a computer.

The kinetic experiments were carried out under *pseudo*-first order conditions, where $[\text{CH}_3\text{CHO}]_0, [\text{H}_2\text{O}_2]_0 \gg [\text{OH}]_0$. Under these conditions and considering the above reaction scheme (R3-5), the integrated rate equation in terms of LIF intensities (I_{LIF}), after rotational relaxation within the OH electronic ground state, is a single exponential.

$$I_{\text{LIF}}(t) = I_{\text{LIF}}(t = 0)\exp(-k't) \quad (1)$$

In Fig. 1, an example of the I_{LIF} temporal profile registered at 45.3 K is shown. The black dots represent the I_{LIF} in absence of CH_3CHO , which correspond to the OH loss by reactions R4 and R5. The red squares represent I_{LIF} in presence of a CH_3CHO concentration of $2.76 \times 10^{13} \text{ molecules cm}^{-3}$. In Fig. 1, the residual I_{LIF} after fitting the experimental data to an exponential decay is shown in the upper panel. From the analysis of these exponential decays of the LIF signal, the *pseudo*-first order rate coefficient, k' , was obtained at several initial acetaldehyde concentrations, $[\text{CH}_3\text{CHO}]_0$, which were varied by changing the mass flow rate of a diluted mixture containing a well-known quantity of CH_3CHO .

The values of k' depend on the $[\text{CH}_3\text{CHO}]$ as follows:

$$k' = k(T)[\text{CH}_3\text{CHO}] + k'_0 \quad (2)$$

where k'_0 is the *pseudo*-first order rate coefficient in the absence of acetaldehyde, *i.e.* the loss rate of OH due to reaction with H_2O_2 and other processes, such as diffusion out of the detection zone. From the slope of k' versus $[\text{CH}_3\text{CHO}]$, the rate coefficient for the gas-phase reaction, $k(T)$, is obtained at a given temperature and total pressure. Since k'_0 fluctuates sometimes from one series of measurements to another one, plots of $k' - k'_0$ versus $[\text{CH}_3\text{CHO}]$ are presented in Fig. 2 in order to compare or aggregate various experiments carried out within the same flow conditions.

$$k' - k'_0 = k(T)[\text{CH}_3\text{CHO}] \quad (3)$$

The error bars in $k' - k'_0$ represent the standard deviation of the propagated uncertainties in k' and k'_0 derived from the fit of the LIF OH decays. Error bars in $[\text{CH}_3\text{CHO}]$ are the uncertainties derived from the measurement of the concentration by UV spectroscopy (see ESI). At the very low laser fluences used in this work, the loss of CH_3CHO by photolysis at 248 nm is insignificant. For example, using the absorption cross section of CH_3CHO from Martinez *et al.*⁷⁰ and the quantum yields provided by Morajkar *et al.*⁷¹ at 248 nm and 298 K, the acetaldehyde loss for the maximum concentration used in our experiments ($4.11 \times 10^{14} \text{ molecule cm}^{-3}$) was estimated to be 0.0012%.

Determination of $[\text{CH}_3\text{CHO}]$ by UV spectroscopy

The acetaldehyde concentration in the jet, $[\text{CH}_3\text{CHO}]$, is calculated as the fractional contribution of CH_3CHO in the total flow taking into account the total gas density provided by the buffer gas (n), the dilution factor of acetaldehyde in the storage bulb ($f_{\text{CH}_3\text{CHO}}$), the mass flow rate of diluted CH_3CHO ($F_{\text{CH}_3\text{CHO}}$) and the total mass flow rate through the reactor (F_{total}):

$$[\text{CH}_3\text{CHO}] = \frac{F_{\text{CH}_3\text{CHO}}}{F_{\text{total}}} n f_{\text{CH}_3\text{CHO}} \quad (4)$$

During the kinetic experiments, the mass flow rate of the diluted mixture containing CH_3CHO is changed to vary $[\text{CH}_3\text{CHO}]$. For that reason, in order to keep the OH-precursor concentration and the total mass flow rate constant, the buffer gas flow rate (F_{buffer}) is adjusted to compensate that change and to keep the *reservoir* pressure (P_{res}) and chamber pressure (P_{ch}) constant.

As indicated previously in section 1.3., the mass flow rates are well-known as the mass flow controllers are regularly calibrated, n is obtained from the Pitot tube measurements and $f_{\text{CH}_3\text{CHO}}$ is calculated from partial pressure measurements ($=P_{\text{CH}_3\text{CHO}}/P_{\text{T}}$, where P_{T} is the total pressure in the storage bulb). Since $[\text{CH}_3\text{CHO}]$ has to be accurately known to determine a reliable $k(T)$, the dilution factor $f_{\text{CH}_3\text{CHO}}$ was checked off-line by recording the UV spectrum ($\lambda = 230\text{-}360\text{ nm}$) of several samples of diluted acetaldehyde from the storage bulb at room temperature. Two setups were used to record the UV spectra of acetaldehyde samples from the storage bulb at several total pressures in the UV cell ($P_{\text{UVcell}} = 27 - 533\text{ mbar}$ of diluted acetaldehyde). One recently developed setup consisting in a 20-cm absorption cell irradiated with a deuterium light source (StellarNet, Model SL4 DT-2000) has been used in this work. The transmitted light was detected by a charge-coupled device (CCD) detector (2048 pixels) after the light dispersion in a concave grating (StellarNet, Model Black-Comet BLK-C). This CCD has pre-set calibrations in the whole wavelength range. On the other hand, the experimental UV system used in previous works from our group^{66, 72–74} was also employed for comparison purposes. A 30-W deuterium lamp (Oriel, model Q Series Low Power) irradiated the gas (introduced in a 107 cm jacketed absorption cell) and focused the transmitted light to a 0.5 m spectrometer (Chromex 500is/ms). The radiation was dispersed by a grating (300 grooves/mm with a spectral resolution of 0.19 respectively) and detected by a CCD detector (Andor, model DB401-UV, $1024 \times 128\text{ pixel}^2$) cooled to $-20\text{ }^\circ\text{C}$. In this system, wavelengths were daily calibrated using a Hg/Ar pen ray lamp (Oriel, model 6060).

The values of $f_{\text{CH}_3\text{CHO}}$ in the storage bulb were obtained by comparison of the experimental UV spectrum ($A_{\lambda,\text{exp}}$ versus λ) with a reference acetaldehyde spectrum ($A_{\lambda,\text{ref}}$ versus λ) built using the absorption cross sections (σ_{λ} in base e) recommended by the Jet Propulsion Laboratory⁷⁵ and a concentration of 10^{17} cm^{-3} ($[\text{CH}_3\text{CHO}]_{\text{ref}}$) according to the Beer-Lambert law:

$$A_{\text{I,ref}} = \sigma_{\text{I}} l [\text{CH}_3\text{CHO}]_{\text{ref}} \quad (5)$$

where l is the well-known optical length (20 cm or 107 cm). In Fig. 3(a), the reference spectrum of CH_3CHO is shown together with two UV spectra of diluted acetaldehyde from the bulb. The ratio between the experimental and reference spectra is given by equation 6.

$$\frac{A_{\lambda,\text{exp}}}{A_{\lambda,\text{ref}}} = \frac{[\text{CH}_3\text{CHO}]_{\text{exp}}}{[\text{CH}_3\text{CHO}]_{\text{ref}}} \quad (6)$$

From the slope of the plot of $A_{\lambda,\text{exp}}$ versus $A_{\lambda,\text{ref}}$, the acetaldehyde concentration in the absorption cell, $[\text{CH}_3\text{CHO}]_{\text{exp}}$, is obtained. As shown in Fig. 3(b) excellent linear plots are obtained leading confidence to the determined acetaldehyde concentration and, therefore, the determined dilution factor calculated from equation 7:

$$[\text{CH}_3\text{CHO}]_{\text{exp}} = f_{\text{CH}_3\text{CHO}} \frac{P_{\text{UVcell}}}{RT} \quad (7)$$

The difference between $f_{\text{CH}_3\text{CHO}}$ calculated from the partial pressure of acetaldehyde introduced in the storage bulb and that obtained from spectroscopic measurements was less than 8%, leading confidence in the $[\text{CH}_3\text{CHO}]$ in the jet calculated from $f_{\text{CH}_3\text{CHO}}$ from pressure measurements. To be conservative, the uncertainty in $[\text{CH}_3\text{CHO}]$ presented in Table S1 in the ESI† is considered to be $\pm 10\%$, shown as error bars in concentration in Fig. 2.

Chemicals

Buffer gases: He, Ar and N_2 , all of them with purities of 99.999% (Nippon Gases Europe) were used as supplied. Liquid acetaldehyde (99.5%, Sigma-Aldrich) was degassed by repeated freeze-pump-thaw cycles prior to use. An aqueous solution of hydrogen peroxide (Sigma-Aldrich, initially at 50% w/w) was pre-concentrated as described previously.^{72, 74, 76–78} The H_2O_2 bubbler was stored in the refrigerator at 4 °C after use to avoid thermal decomposition.

Results and Discussion

Temperature dependence of the rate coefficient, $k(T)$

The kinetic measurements were performed at 26 different temperatures ranging between 11.7 K and 177.5 K using 7 Laval nozzles which operate with He, N_2 , Ar or binary mixtures of Ar- N_2 or He- N_2 as bath gases. Further details of the methodology and procedures can be found in Jiménez *et al.*⁶⁸

In Table 2, the measured rate coefficients are listed together with the total gas density of the jet at every temperature (T). Uncertainties on the rate coefficients are $\pm 1\sigma$ statistical errors. Data are plotted in Fig. 4 where a significant increase (more than one order of magnitude) of $k(T)$ can be observed when the temperature decreases from 177.5 down to 21 K. Nevertheless, $k(T < 21 \text{ K})$ is found almost constant, within the uncertainties. This levelling out of $k(T)$ has been already observed for several radical-neutral reactions previously investigated at temperatures below 50 K, such as for instance $\text{CN} + \text{C}_2\text{H}_2$,⁷⁹ $\text{CH} + \text{CH}_4$,⁸⁰ $\text{C}_4\text{H} + \text{C}_3\text{H}_8$,⁸¹ $\text{C}_4\text{H} + \text{C}_3\text{H}_6$,⁸² or $\text{OH} + \text{CH}_3\text{OH}$.⁶³ A reasonable explanation for this behaviour is that the rate coefficient reaches the capture limit.

Previous results from Vöhringer-Martinez *et al.*⁴¹ are also presented in Fig. 4. They were found to be about 60% lower than those obtained in the present study. In their main paper,

Vöhringer-Martinez *et al.*⁴¹ showed the evolution of the decay of the OH LIF intensity at 77 K as a function of time, through which the *pseudo*-first order rate coefficient (k') was determined. In order to observe a significant LIF decay in their short time-scale (about 100 μ s), such as exemplified in Figure 1B of Vöhringer-Martinez *et al.*'s paper,⁴¹ they introduced a fairly high concentration of acetaldehyde. However, at the low temperatures of this kind of experiments, high concentrations of reagents may initiate dimerisation (and further clustering) resulting in a downward curvature of the bimolecular plots. This topic was recently discussed for the OH+methanol reaction.^{63, 83, 84} Figure 1C from Vöhringer-Martinez *et al.* shows the k' versus $[\text{CH}_3\text{CHO}]$ plot at 77 K. At first sight and without knowing the experimental k'_0 value, which is not plotted, the linear fit looks acceptable, although some curvature could be appreciated. In the present work, one of our flow conditions corresponded to a temperature of 76 K allowing thus a direct comparison with Vöhringer-Martinez *et al.*'s results at 77 K. As shown in Fig. S4 in the ESI†, at 76 K the gas flow presents a great spatial stability, offering a time-scale of 918 μ s for the kinetic measurements. Taking advantage of this favourable situation, in the present work much lower $[\text{CH}_3\text{CHO}]$ ($(0.03\text{--}0.26)\times 10^{14} \text{ cm}^{-3}$) than those of Vöhringer-Martinez *et al.*, $(0.25\text{--}2.5)\times 10^{14} \text{ cm}^{-3}$ were used. In Fig. 5, the *pseudo*-first order rate coefficients obtained in this work as a function of $[\text{CH}_3\text{CHO}]$ are compared with Vöhringer-Martinez *et al.*'s data. The inset plot in Fig. 5 is a zoom of our results, where only the data represented by filled circles are taken into account in the linear fit to equation 2. Data represented by hollow circles are then discarded for the rate coefficient determination due to curvature of the plot. Since the *pseudo*-first order rate coefficient in absence of acetaldehyde (k'_0) mainly depends on the H_2O_2 concentration (OH-precursor used also by Vöhringer-Martinez *et al.*), the comparison shown in Fig. 5 requires that our k'_0 and, therefore, k' values were scaled by an offset. The k'_0 offset was selected so that their data and ours match at a concentration of around $3\times 10^{13} \text{ cm}^{-3}$, *i.e.* the lowest CH_3CHO concentration of Vöhringer-Martinez *et al.* and the concentration beyond which curvature was observed in our study. As seen in Fig. 5, the slope of our data (black line, $k = (9.42 \pm 1.04) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), is about twice higher than the one obtained by Vöhringer-Martinez *et al.* (red line). The lowest concentration used by Vöhringer-Martinez *et al.* more or less coincides with the onset of CH_3CHO dimerisation, since their measurements clearly depart from the linearity observed in our experiments. This strongly suggests that Vöhringer-Martinez *et al.* did not measure the rate coefficient between OH and CH_3CHO molecules, but instead the total removal of OH in the presence of a mixture of the monomer and CH_3CHO clusters, whose concentration increase as the acetaldehyde percentage was increased in the flow. This fact provokes an underestimation of $k(T)$.

At the rest of temperatures explored by Vöhringer-Martinez *et al.*⁴¹ (60, 106 and 118 K), the acetaldehyde concentration range (see their SI document) was always found to be significantly higher than ours. Therefore, it is very likely that a large amount of acetaldehyde dimers be present in their experiments and this can be the source of the observed discrepancy, as well at those temperatures.

In this work, $k(T)$ were fitted to a three-parameters modified Arrhenius equation recommended for modelling the observed abundances of interstellar species.⁸⁵

$$k(T) = \alpha \left(\frac{T}{300} \right)^\beta \exp\left(\frac{-\gamma}{T}\right) \quad (8)$$

The parameters obtained from the fit to equation 8 are $\alpha = (1.2 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $\beta = -(1.8 \pm 0.1)$ and $\gamma = (28.7 \pm 2.5) \text{ K}$, where uncertainties are $\pm 1\sigma$ statistical error of the fitting.

At temperatures higher than 200 K, there are many studies on the temperature dependence of $k(T)$.^{41–5} In Fig. 6, our results are presented together with those reported in the literature^{41–46, 48–50} and the IUPAC recommendation for the temperature dependence of $k(T)$ between 200 and 380 K.⁸⁶ It should be noted that for the OH+CH₃CHO reaction the T -dependence of $k(T)$ changes from a negative dependence below around 600 K to a positive T -dependence at T higher than 600 K as reported by Taylor *et al.*⁴⁷ The change in the temperature dependence of $k(T)$ has been also observed for other OH-reactions and it usually happens at temperatures around 200 K^{62, 63, 65, 67} or even at room temperature.⁶⁶

Pressure dependence of $k(T)$

For a given target temperature obtained in a supersonic flow it is not possible to tune the flow pressure as it can be easily done in a static or slow flow cell. Doing so would destroy the uniformity of the supersonic flow downstream of the nozzle because the constraint of equality between the flow pressure P (within the isentropic core) and the static pressure in the chamber (P_{ch}) would not be respected any more. Hence, usually a dedicated new nozzle contour has to be designed for a flow at the same target temperature and different pressure. Alternatively, quite often, an existing nozzle working at different flow conditions (gas, mass flow rate, T , P) can be “reconditioned” in order to work at the desired target temperature. This leads to a new set of working conditions in terms of gas, mass flow rate and flow pressure which must obviously match with the geometry of that nozzle.⁶⁹ The Laval nozzles available in our group made this possible in many situations. Consequently, rate coefficient determinations could have been carried out at different pressures at approximately the same temperature, *i.e.* at *ca.* 21, 50, 64 and 106 K using different Laval nozzles and/or different bath gases, as shown in Tables 2 and S1 in the ESI†, and in Fig. 7.

In the investigated pressure range, no dependence was found in any case. This observation agrees with the experimental work from Sivakumaran and Crowley,⁴⁸ who also found no pressure dependence of the rate coefficient measured at room temperature and either 50 or 100 Torr of He or Ar bath gas. Further, the calculations carried out by Vöhringer-Martinez *et al.*⁴¹ show that the title reaction proceeds *via* initial formation of an intermediate pre-reactive complex CH₃CHO...OH separated from the main products CH₃CO + H₂O by a submerged transition state barrier. They also claimed that the intermediate, even up to pressures of 1 bar, cannot be collisionally stabilized and concluded that the OH+CH₃CHO reaction was in its low-pressure limit under their experimental conditions. The present results have been obtained at pressures of typically 1 mbar and then the pre-reactive complex is left to either redissociate back to reactants or pass over the submerged barrier. At the very low temperatures of our study, redissociation is certainly negligible with respect to the

forward mechanism leading to product formation. Hence, the observations that $k(T)$ is pressure independent under our experimental conditions is not surprising.

Error analysis

The uncertainties in T , n and P showed in Tables 2, S1 and S2 in the ESI† are not strictly speaking uncertainties. They represent the fluctuations of the physical conditions of the jet along with its expansion, as exemplified in Fig. S1-S4 in the ESI†. On the other hand, the uncertainties in the rate coefficients reported in Table 2 are the statistical error ($\pm 2\sigma$) derived from the slope of the second-order plots, $k' - k'_0$ versus $[\text{CH}_3\text{CHO}]$, such as those shown in Fig. 1. Nonetheless, the total uncertainty includes the systematic errors due to potential instrumental biases, for instance, deviation from the initial calibration of mass flow controllers or pressure gauges. We estimate that systematic error does not exceed 10% of the measured rate coefficient values, as it has been already been observed in other works in our laboratory.^{62, 63, 65, 66} Therefore, the total uncertainty in $k(T)$ has been calculated as the square root of the sum of the systematic error and the $\pm 2\sigma$ statistical error squared. The total uncertainties of $k(T)$ are shown as error bars in Fig. 4 and 7.

Astrophysical implications

At the very low temperatures found in the cold molecular clouds of the ISM, a value of $3.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (representative of the present data for the $\text{OH} + \text{CH}_3\text{CHO}$ reaction at low temperatures) was used for modelling the impact of the title reaction in the formation of CH_3CO radicals (Fig. 8). We have considered that the branching ratio towards $\text{CH}_3\text{CO} + \text{H}_2\text{O}$ (R1) is 100% based on the theoretical calculations lead by Vöhringer-Martinez *et al.*⁴¹ We adopted typical parameters of cold dark clouds, *i.e.*, a gas kinetic temperature of 10 K, a volume density of H nuclei of $2 \times 10^4 \text{ cm}^{-3}$, a visual extinction of 30 mag, and a cosmic-ray ionization rate of H_2 of $1.3 \times 10^{-17} \text{ s}^{-1}$. Also, a set of “low-metal” elemental abundances, in which the abundances of metals, Si and S are depleted with respect to the values observed in the diffuse cloud $\zeta \text{ Oph}$ (see, *e.g.* Agúndez & Wakelam⁸⁷). The two most widely used chemical networks in interstellar chemistry, *kida.uva.2014* from the KIDA database⁸⁵ and *rate.2012* from the UMIST database,⁸⁸ lack of reactions involving the CH_3CO radical, which is the most obvious product of the reaction between OH and CH_3CHO , studied here. We have therefore adopted these two chemical networks adding a subset of reactions involving the CH_3CO radical, which are listed in the KIDA database, but are not included in the chemical network *kida.uva.2014*. Within this subset of reactions, the reaction between OH and CH_3CHO is listed in the KIDA database with a rate coefficient of $1.42 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, reported by Tyndall *et al.*³⁷ at room temperature. This rate coefficient is 26 times lower than those measured in this work below 22 K. Other reactions, such as $\text{H} + \text{CH}_3\text{CHO}$, are negligible sources of CH_3CO since they have activation barriers that make them too slow at the low temperatures of the ISM or because the abundance of the involved reactants are too low, making the reaction rate too slow.

In Fig. 8, we show the calculated abundances for CH_3CHO and CH_3CO as a function of the evolving time for a cold dark cloud, using either the KIDA or UMIST chemical networks, in both cases the predicted abundances augmented with the subset of chemical reactions. It is seen that when the rate coefficient of the reaction $\text{OH} + \text{CH}_3\text{CHO}$ is increased from the

value listed in KIDA, from $1.42 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $3.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, the abundance of CH_3CO increases by more than one order of magnitude. The model indicates that the reaction $\text{OH} + \text{CH}_3\text{CHO}$ is the main formation route for CH_3CO in cold dark clouds. Still, the predicted peak abundance of CH_3CO remains below 10^{-13} relative to total H nuclei, which is probably too small to be observed with current radiotelescopes.

The relative CH_3CO abundances obtained for a typical dense cloud are, therefore, an upper limit, since as indicated by Howes *et al.*,⁵¹ the excited CH_3CO formed in reaction (R1) can partially dissociate to CH_3 and CO (Note that this result is for room temperature). This process was found to be pressure dependent, as collisions with the neighbouring molecules can stabilize the CH_3CO radical. At zero pressure, the branching ratio towards CH_3 formation was reported to be in the range 12-20%.⁵¹ In the ISM, pressure is considerably lower than in usual laboratory chambers. Consequently, it is unlikely that collisions contribute significantly to stabilize the excited CH_3CO and then it is sensible to assume that some CH_3 would be formed as well in such low temperature conditions. Further, if the time scale is sufficiently long between two collisional events, tunnelling-decomposition from medium-excited CH_3CO can also play a role. The real yield towards stabilized CH_3CO in the ISM conditions, and more specifically in a dense cloud, is therefore likely to be lower than 80%. Reducing the CH_3CO yield in our model would not alter the final conclusion since the new predicted abundance would still be lower than the sensitivity of the present observational tools.

Conclusions

We have experimentally measured the rate coefficient of the reaction between the OH radical and acetaldehyde in the temperature range of 11.7 – 177.5 K using laser techniques coupled to a CRESU apparatus. This work constitutes the first experimental determination of the rate coefficient $k(T)$ below 60 K, highly interesting for modelling of interstellar chemistry.

As no pressure-dependence of $k(T)$ at *ca.* 21, 50, 64 and 106 K was observed, in agreement with theoretical calculations, the title reaction has been investigated in the low-pressure limit in this work. The recommended modified Arrhenius parameters for modelling the ISM chemistry of CH_3CHO are: $\alpha = (1.2 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $\beta = -(1.8 \pm 0.1)$ and $\gamma = (28.7 \pm 2.5) \text{ K}$.

Using the average experimental rate coefficients at the lowest temperatures, the gas-phase chemical model indicates that the reaction $\text{OH} + \text{CH}_3\text{CHO}$ is the main formation route for CH_3CO in cold dark clouds although the abundance of this radical is probably too small to be observed in those cold environments of the ISM with current radiotelescopes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.

Example of the temporal profile of the OH LIF signal recorded at 45.3 K.

Fig. 2.
Examples of $k' - k_0$ versus acetaldehyde concentration plots at several temperatures ($k(T)$ in $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ units).

Fig. 3.

(a) Examples of the UV spectrum of CH_3CHO from the storage bulb at four different concentrations of acetaldehyde; (b) Plot of equation 7 for data presented in the upper panel.

Fig. 4.

Temperature dependence of the rate coefficient for the OH + CH₃CHO reaction in the range of 11.7 to 177.5 K found in this work and comparison with previous data (Vöhringer-Martinez *et al.*⁴¹). The grey area represents the upper and lower limits of the fit.

Fig. 5. Example of the plot of the pseudo-first order rate coefficient versus CH_3CHO concentration at *ca.* 77.0 K. The inset plot emphasizes the present data in the linear range (black circles) and in the curved area (white circles).

Fig. 6.
Temperature dependence of $k(T)$ for the $\text{OH} + \text{CH}_3\text{CHO}$ reaction between 11.7 and 1400 K.

Fig. 7. Dependence of the rate coefficient $k(T)$ as a function of density at (a) *ca.* 21 and 50 K, and (b) *ca.* 64 and 106 K. The bath gas (or mixture) used is indicated at each point. Error bars in $k(T)$ and n are the total uncertainty.

Fig. 8. Relative abundance to total H nuclei of CH_3CO and CH_3CHO as a function of evolving time using (a) KIDA and (b) UMIST databases. Dashed lines represent the modelled abundances using the rate coefficient for $\text{OH}+\text{CH}_3\text{CHO}$ reaction from KIDA database, while the solid lines represent those using the rate coefficient obtained in this work.

Table 1

Observed column densities of CH₃CHO ($N_{\text{CH}_3\text{CHO}}$) and relative abundances to H₂ ($N_{\text{CH}_3\text{CHO}}/N_{\text{H}_2}$) in different astrophysical sources.

Source	$N_{\text{CH}_3\text{CHO}} / \text{cm}^{-2}$	$N_{\text{CH}_3\text{CHO}}/N_{\text{H}_2}$	Reference
TMC-1	6×10^{12}	6×10^{-10}	7, 8
Hot corino of SVS13-A	$(5-19) \times 10^{15}$	$(1.7-6.3) \times 10^{-9}$	9
HH212 hot corino	2×10^{15}	$(0.2-2) \times 10^{-9}{}^a$	10
L134N	6×10^{12}	6×10^{-10}	8
Sagittarius B2(N)	$(<1.5-5) \times 10^{13}$	$(<5.2-17) \times 10^{-12}{}^b$	11–15
OMC2-IRS4	5.2×10^{12}	$1.0 \times 10^{-10}{}^c$	18
Orion-KL	1.2×10^{13}	$4.0 \times 10^{-11}{}^d$	18
WL22	3.4×10^{12}	1.7×10^{-10}	18
NGC 6334I	2.9×10^{14}	$1.5 \times 10^{-9}{}^d$	18
G34.26	3.1×10^{14}	$1.0 \times 10^{-9}{}^d$	18
W51M	4.1×10^{12}	$1.1 \times 10^{-11}{}^d$	18
DR21(OH)	1.4×10^{13}	$1.4 \times 10^{-10}{}^d$	18
W3(OH)	4.1×10^{12}	$4.3 \times 10^{-11}{}^d$	18
CKI	4.8×10^{12}	$9.6 \times 10^{-11}{}^e$	18

NH₂ from:

^aTaquet *et al.*²¹;

^bSchmiedeke *et al.*²²;

^cBatrla *et al.*²³;

^dIkeda *et al.*²⁴;

^eHogerheijde *et al.*²⁵

Table 2Experimental rate coefficients $k(T)$ ($\pm 2\sigma$ statistical) as a function of temperature and gas density.

$\sim T/K$	T/K	$n/10^{16}\text{cm}^{-3}$	$k(T)/10^{-11}\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
	11.7 ± 0.7	6.88 ± 0.62	33.7 ± 3.7
	13.0 ± 0.7	6.41 ± 0.55	37.2 ± 4.4
	14.6 ± 1.0	4.98 ± 0.51	34.0 ± 3.2
	18.6 ± 0.6	5.53 ± 0.25	37.0 ± 5.7
21	21.1 ± 0.6	3.37 ± 0.15	38.1 ± 4.4
	22.5 ± 0.7	7.43 ± 0.32	33.9 ± 3.5
	21.7 ± 1.4	16.7 ± 1.6	37.1 ± 4.1
	26.9 ± 1.1	4.08 ± 0.26	26.5 ± 1.8
	36.2 ± 1.2	17.7 ± 0.9	20.5 ± 1.4
	45.3 ± 1.3	4.23 ± 0.28	18.3 ± 2.6
50	50.5 ± 1.6	1.50 ± 0.12	15.8 ± 1.9
	51.6 ± 1.7	4.17 ± 0.35	14.6 ± 2.3
	49.9 ± 1.4	8.33 ± 0.41	19.6 ± 2.7
	52.1 ± 0.5	19.5 ± 0.3	15.4 ± 5.4
64	64.2 ± 1.7	2.23 ± 0.15	12.4 ± 0.8
	64.1 ± 1.6	4.63 ± 0.27	12.2 ± 1.6
	64.4 ± 0.6	17.4 ± 0.3	12.8 ± 1.9
	76.0 ± 0.8	15.0 ± 0.3	9.42 ± 1.04
	89.5 ± 0.6	18.2 ± 0.3	7.57 ± 0.29
106	107.0 ± 0.5	4.90 ± 0.06	5.36 ± 0.77
	106.0 ± 0.6	14.0 ± 0.1	5.27 ± 0.62
	115.3 ± 1.1	9.58 ± 0.14	4.80 ± 0.32
135	135.0 ± 0.8	29.4 ± 0.5	3.75 ± 0.27
	136.1 ± 0.8	24.9 ± 0.4	3.95 ± 0.30
	158.8 ± 0.6	7.40 ± 0.07	3.05 ± 0.11
	177.5 ± 1.2	6.71 ± 0.11	2.60 ± 0.06