Gas-phase reactivity of OH radicals with ammonia (NH_3) and methylamine (CH_3NH_2) at around 22 K

Daniel González[1], Bernabé Ballesteros[1,2], André Canosa[3], José Albaladejo[1,2] and Elena Jiménez[1,2,*]

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

[2]Instituto de Investigación en Combustión y Contaminación Atmosférica, UCLM, Camino de Moledores s/n, 13071 Ciudad Real, Spain.

[3] Institut de Physique de Rennes-CNRS – UMR 6251, Université de Rennes, F-35000 Rennes, France.

*** Correspondence:**
Elena.Jimenez@uclm.es

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Abstract

Interstellar molecules containing N atoms, such as ammonia (NH_3) and methylamine (CH_3NH_2), could be potential precursors of amino acids like the simplest one, glycine (NH_2CH_2COOH). The gas-phase reactivity of these N-bearing species with OH radicals, ubiquitous in the interstellar medium, is not known at temperatures of cold dark molecular clouds. In this work, we present the first kinetic study of these OH-reactions at around 22 K and different gas densities ((3.4-16.7)×10^{16} cm^{-3}) in helium. The obtained rate coefficients, with ±2σ uncertainties,

$k_1(OH+NH_3) = (2.7\pm0.1)\times10^{-11}$ cm^3 s^{-1}

$k_2(OH+CH_3NH_2) = (3.9\pm0.1)\times10^{-10}$ cm^3 s^{-1}

can be included in pure gas-phase or gas-grain astrochemical models to interpret the observed abundances of NH_3 and CH_3NH_2. We observed an increase of k_1 and k_2 with respect to those previously measured by others at the lowest temperatures for which rate coefficients are presently available: 230 K and 299 K, respectively. This increase is about 380 times for NH_3 and 20 times for CH_3NH_2. Although the $OH+NH_3$ reaction is included in astrochemical kinetic databases, the recommended temperature dependence for k_1 is based on kinetic studies at temperatures above 200 K. However, the $OH+CH_3NH_2$ reaction is not included in astrochemical networks. The observed increase in k_1 at ca. 22 K does not significantly change the abundance of NH_3 in a typical cold dark **interstellar** cloud. However, the inclusion of k_2 at ca. 22 K, not considered in astrochemical networks, indicates that the contribution of this destruction route for CH_3NH_2 is not negligible, accounting for 1/3 of the assumed main depletion route (reaction with HCO^+) in this IS environment.

Introduction

Unravelling the origin of life on the Earth has been both a challenge and a matter of debate for scientists throughout the history. However, what we can be certain about is that all ingredients essential for life are composed by a few atoms such as H, O, C, N, or S. The combination of these atoms can produce different prebiotic molecules, which are considered the precursors of life on our planet. Principally, two main theories have been proposed for trying to explain how these molecules could have appeared on the globe (Chyba and Sagan, 1992; Bernstein, 2006). The first one states that the organic molecules that serve as the basis of life were formed in the primitive atmosphere of our planet from simpler and smaller molecules (*e.g.* NH_3, CH_4, H_2O, or H_2) (Miller, 1953; Bada and Lazcano, 2002; Cleaves et al., 2008). In fact, this was demonstrated experimentally by Stanley Miller in the middle of the past century when he obtained a considerable number of important compounds from the biological point of view, such as amino acids, from simple molecules like the aforementioned, after exposing them to conditions aiming at mimicking those reigning in the primitive Earth (Miller, 1953). The second one is based on the idea that the prebiotic molecules were firstly synthesized in space and then, they could have been delivered to the Earth by meteorites, comets, asteroids or even interplanetary dust particles (Ehrenfreund et al., 2002; Sandford et al., 2020). This latter hypothesis is now in trend due to the huge and unexpected discovery in the last 70 years of the chemical richness in the interstellar medium (ISM). Currently, about 250 species (including ions and neutrals) have been detected in the ISM or circumstellar shells (Woon, 2021). Interstellar molecules, which are found in ultra-cold environments (~10-100 K), such as the so-called dense or dark clouds or pre-stellar cores, range from simple diatomic molecules (*e.g.* CO or the hydroxyl (OH) radical) to more complex systems (*e.g.* fullerenes). For instance, the OH radical, firstly detected in Cassiopeia A in 1963 (Weinreb et al., 1963), is ubiquitous in the ISM. By definition, carbon-bearing species containing 6 atoms or more are called complex organic molecules (COMs) (Herbst and van Dishoeck, 2009). Some COMs containing C-O bonds (such as CH_3OH) and C-N bonds (such as CH_3CN) can be potential precursors of sugars and amino acids in the presence of water, respectively (Balucani, 2009), under the Earth's conditions. Although ammonia (NH_3) is not considered a COM, strictly by definition, this abundant nitrogen-bearing species is very important since it serves as temperature probe in molecular clouds like Sagittarius (Sgr) B2, where it was first detected (Cheung et al., 1968). Ammonia has also been found towards a post-star forming region, W3(OH), with an abundance relative to H_2 of 10^{-8} (Wilson et al., 1993) and in TMC-1, with a column density of $\sim 10^{15}$ cm^{-2} (Freeman and Millar, 1983). Another interesting N-bearing species is methylamine (CH_3NH_2), which was detected in the 1970s years for the first time towards Sgr B2 and Orion A (Fourikis et al., 1974; Kaifu et al., 1974). Abundances relative to H_2 for CH_3NH_2 have been observed to be 10^{-8} towards the hot core G10.47+0.33 (Ohishi et al., 2019) and 10^{-9} for Sgr B2 (Halfen et al., 2013). Both NH_3 and CH_3NH_2 have been proposed as precursors of the simplest amino acid, glycine (NH_2CH_2COOH), through H-atom abstraction reactions forming NH_2 (Sorrell, 2001; Garrod, 2013) and CH_2NH_2 radicals, (Woon, 2002; Garrod, 2013); however interstellar glycine remains undetected in the ISM so far.

Under the ISM conditions, it has been assumed since a long time (Herbst and Klemperer, 1973) that dissociative recombination of NH_4^+ is the main provider of NH_3 in the gas phase. This cation can be generated through a series of hydrogen abstraction reactions starting from $N^+ + H_2$ leading step by step to NH^+, NH_2^+, NH_3^+ and eventually NH_4^+ (Gerin et al., 2016; Rednyk et al., 2019). Alternatively, NH_2^+ can be produced by $H_3^+ + N$ (Scott et al., 1997). Although not included in interstellar chemical networks, another potential source of NH_3 was recently claimed by Gianturco *et al.* (2019) to be the reaction of the NH_2^- anion with H_2. Surface reactions have also been proposed as plausible mechanisms to produce ammonia via a series of atomic hydrogen additions to N-hydrides

after NH has been formed through N + H → NH (Jonusas et al., 2020). Regarding CH_3NH_2, different synthetic routes have been proposed. In the gas-phase, it may be formed via the radiative association between NH_3 and the methyl radical cation (CH_3^+) followed by dissociative recombination (Herbst, 1985). But CH_3NH_2 can also be formed on grain surfaces by sequential hydrogenation of hydrogen cyanide (HCN), as experimentally observed by Theule *et al.* (2011). Simulations of the irradiation of CH_4 and NH_3 ices may also form CH_3NH_2 (Kim and Kaiser, 2011; Förstel et al., 2017), but also in cold and quiescent molecular clouds (Ioppolo et al., 2021). In the gas-grain chemical model by (Garrod et al., 2008), the CH_3+NH_2 reaction was also suggested as a source of CH_3NH_2 during warm-up phases.

It is also important to know how NH_3 and CH_3NH_2 are being destroyed to have a good insight of the chemical evolution of the ISM. Focusing on neutral-neutral reactions, reaction networks that astrochemical models used, such as KIDA and UDfA, include eight depletion routes for NH_3. *e.g.* reactions with H, CH, CN, among other radicals. Concerning CH_3NH_2, only two depleting reactions by CH and CH_3 radicals are included in KIDA database, while UDfA database does not include any. Until now, the reactivity of NH_3 with neutral radicals or atoms at ISM temperatures has been investigated experimentally in the presence of CN (Sims et al., 1994), CH (Bocherel et al., 1996), C_2H (Nizamov and Leone, 2004) and C(^{3}P) (Bourgalais et al., 2015; Hickson et al., 2015) whereas, only the reactivity of CH_3NH_2 with CN is documented (Sleiman et al., 2018a, 2018b). Due to the important role of OH radicals as a key intermediate in multiple reactive processes in the ISM (Cazaux et al., 2010; Goicoechea et al., 2011; Acharyya et al., 2015; Linnartz et al., 2015), the kinetic database for OH-molecule reactions has been widely extended in the past years (see e.g. Taylor et al., 2008; Smith and Barnes, 2013; Ocaña et al., 2017, 2019; Potapov et al., 2017; Heard, 2018; Blázquez et al., 2019, 2020). For the OH+NH_3 reaction (Reaction R1), of interest in atmospheric and combustion chemistry, its gas-phase kinetics has been extensively studied both experimentally and theoretically.

$$OH + NH_3 \rightarrow H_2O + NH_2 \qquad k_1 \qquad \text{(R1)}$$

Note that other reaction channels forming H_2NO+H_2, HNOH+H_2, or H_2NOH+H are not thermodynamically accessible, since they are endothermic by Gibbs free energies ranging from 19.67 to 31.73 kcal/mol (Vahedpour et al., 2018). Reaction R1 is also of astrochemical interest since it leads to the formation of NH_2 radicals, which were also observed towards the same location as ammonia (van Dishoeck et al., 1993). In the laboratory studies, the rate coefficient for R1, k_1, has been reported since the 1970's by many research groups over a wide range of temperature (230-2360 K) and pressures (1-4000 mbar) (Stuhl, 1973; Kurylo, 1973; Zellner and Smith, 1974; Hack et al., 1974; Perry et al., 1976; Silver and Kolb, 1980; Fujii et al., 1981, 1986; Salimian et al., 1984; Stephens, 1984; Zabielski and Seery, 1985; Jeffries and Smith, 1986; Diau et al., 1990). A summary of all previous experimental results can be found in Diau *et al.* (1990). The observed dependence of k_1 with temperature is positive, *i.e.*, the rate coefficient increases when temperature increases, and the reported activation energies range from 0.5 to 9 kcal/mol in the 230-2360 K range (Zellner and Smith, 1974; Hack et al., 1974; Perry et al., 1976; Silver and Kolb, 1980; Fujii et al., 1981, 1986; Salimian et al., 1984; Stephens, 1984; Zabielski and Seery, 1985; Jeffries and Smith, 1986; Diau et al., 1990). The computed energy barriers in the 200-4000 K range were found to be between 2.0 and 9.05 kcal/mol (Giménez et al., 1992; Corchado et al., 1995; Bowdridge et al., 1996; Nyman, 1996; Lynch et al., 2000; Monge-Palacios et al., 2013b; Nguyen and Stanton, 2017). The reaction mechanism of R1 was also theoretically investigated (Giménez et al., 1992; Espinosa-García and Corchado, 1994; Corchado et al., 1995; Bowdridge et al., 1996; Nyman, 1996; Lynch et al., 2000; Monge-Palacios et al., 2013b; Nguyen and Stanton, 2017). The formation of a pre-reactive complex

(PRC) at the entrance channel is accepted, as illustrated in Scheme 1, and quantum mechanical tunneling has been reported to be an important contribution to k_1, leading to the observed non-Arrhenius behavior (Espinosa-García and Corchado, 1994; Corchado et al., 1995; Bowdridge et al., 1996; Nyman, 1996; Monge-Palacios et al., 2013b; Nguyen and Stanton, 2017).

Regarding the OH+CH_3NH_2 reaction (Reaction R2), previous kinetic studies are restricted to temperatures higher than 295 K (Atkinson et al., 1977; Carl and Crowley, 1998; Onel et al., 2013; Butkovskaya and Setser, 2016). From the experimental point of view, Atkinson *et al.* (1977) and Onel *et al.* (2013) reported the temperature dependence of reaction R2 in the 299-426 K and 298-600 K ranges, respectively. A negative temperature dependence of k_2 was observed and this rate coefficient increases when temperature decreases.

$$OH + CH_3NH_2 \rightarrow \text{Products} \qquad k_2 \qquad \text{(R2)}$$

Reaction R2 may proceed by H-abstraction from methyl (-CH_3) or amino (-NH_2) groups forming CH_2NH_2 and CH_3NH radicals plus water, respectively. The formation of CH_2NH_2 radicals was measured to be the main reaction channel at room temperature (Nielsen et al., 2011, 2012; Onel et al., 2014; Butkovskaya and Setser, 2016), in agreement with theoretical predictions at 299 K and above (Galano and Alvarez-Idaboy, 2008; Tian et al., 2009). These calculations suggest a stepwise mechanism involving the formation of a PRC at the entrance channels and an energy barrier of a few kcal/mol for the H-abstraction channel from -CH_3 group, as depicted in Scheme 2.

As there are no kinetic data of k_1 and k_2 at temperatures of the cold dark interstellar clouds and since they are necessary to properly model the chemistry of the ISM, we present in this work the first determination of the rate coefficient for the reactions of NH_3 and CH_3NH_2, k_i (i=1 or 2), with OH radicals at ca. 22 K using a combination of a pulsed CRESU (French acronym for *Reaction Kinetics in a Uniform Supersonic Flow*) reactor with laser techniques. The implications of the reported new rate coefficients will be discussed in terms of their effect on the predicted abundances of NH_3 and CH_3NH_2 in a typical cold dark interstellar cloud at 10 K.

Experimental methods

CRESU apparatus coupled to pulsed laser photolysis-laser induced fluorescence technique

The experimental system based on the pulsed uniform supersonic expansion of a gas mixture has been already described elsewhere (Jiménez et al., 2015, 2016; Antiñolo et al., 2016; Canosa et al., 2016; Ocaña et al., 2017, 2018, 2019; Blázquez et al., 2019, 2020; Neeman et al., 2021). To carry out the kinetic experiments, three Laval nozzles (He23-HP, He23-IP, and He23-LP) were used with helium as a carrier gas. These nozzles were designed to generate a uniform flow at around 22 K for three different jet pressures (see Table 1) (Jiménez et al., 2015; Canosa et al., 2016; Ocaña et al., 2017), thus allowing us to explore the influence of pressure on the reactivity at a constant temperature. Bath gas and reactants (NH_3 or CH_3NH_2) were introduced in the CRESU chamber through calibrated mass flow controllers, MFCs (Sierra Instruments, Inc., model Smart Trak, Smart-Trak 2, MicroTrak 101 and Smart-Trak 100). CH_3NH_2 was diluted in He and stored in a 20-L or 50-L bulb. Calibrated mass flow rates of these diluted mixtures ranged from 6.6 to 200 sccm (standard cubic centimeters per minute), depending on the Laval nozzle used. Dilution factor f ranged from 1.78×10^{-2} to 4.54×10^{-2}. In contrast, NH_3 was flown directly to the pre-expansion chamber (*reservoir*) from a gas cylinder through a MFC manufactured with anticorrosive materials (Sierra Instruments, Inc., model Smart-Trak 100). The flow rates of pure NH_3 ranged from 3 to 15 sccm. The OH-

precursor employed was H_2O_2, since it is a clean source of OH radicals. Gaseous H_2O_2 was introduced into the *reservoir* by bubbling the bath gas through an aqueous solution of H_2O_2, as explained in Jiménez *et al*. (2005). The flow rate of He through the H_2O_2 bubbler in different experiments ranged from 35.6 to 265.8 sccm, depending on the Laval nozzle used. Within a kinetic experiment, this flow rate was kept constant to maintain invariable the contribution of the OH loss due to the OH+H_2O_2 reaction (see kinetic analysis). The gas mixture formed by He (main flow), He/H_2O_2, and the reactant was pulsed by a two holes rotary disk described in Jiménez *et al.* (2015).

After the gas expansion through the Laval nozzle, the jet temperature was measured by a Pitot tube to be (21.7±1.4) K for the He23-HP nozzle, (22.5±0.7) K for the He23-IP nozzle, and (21.1±0.6) K for the He-23LP nozzle, respectively. Within the fluctuation along the flow axis (±σ), the jet temperature in all cases is ca. 22 K. The procedure to determine the jet temperature and gas density has been previously described (Jiménez et al., 2015; Canosa et al., 2016; Ocaña et al., 2017). Pulsed photolysis of H_2O_2(g) at 248 nm was achieved by the radiation coming from a KrF excimer laser (Coherent, model ExciStar XS 200) with energies at the exit of the nozzle ranging from 0.5 to 0.9 mJ/pulse at 10 Hz, depending on the nozzle used. OH radicals were monitored by collecting the laser induced fluorescence (LIF) at 310 nm, after laser excitation at *ca.* 282 nm, as a function of the reaction time defined as the time delay between the probe laser pulse and the excimer one.

Kinetic analysis

In Fig. 1 an example of the temporal evolution of the LIF intensity (I_{LIF}) is presented. As explained in several papers (Jiménez et al., 2015; Ocaña et al., 2018), the observed rise of the I_{LIF} signal at $t>0$ is due to rotational relaxation of OH, coming from H_2O_2 photodissociation, that occurs in a timescale (t_0) of less than 30 μs under the conditions of the experiments, especially, at the concentration levels of the reactant, which is an effective quencher. The fit of the recorded I_{LIF} profiles to an exponential decay (solid lines in Fig. 1) confirms that the OH loss follows a pseudo-first order kinetics.

$$\boldsymbol{I_{LIF}(t) = I_{LIF}(t_0)\ exp^{-k'(t-t_0)}} \qquad \textbf{(E1)}$$

The pseudo-first order rate coefficient, k', includes all the OH loss processes occurring simultaneously in the cold jet.

$$\boldsymbol{k' = k'_0 + k_i[Reactant]} \qquad \textbf{(E2)}$$

where k_i (i=1 or 2) is the bimolecular rate coefficients for OH-reactions with NH_3 (R1) and CH_3NH_2 (R2). In the absence of reactant, k'_0 was measured, and it included the loss of OH radicals by OH-reaction with H_2O_2 and other OH losses, such as diffusion out of the detection zone. In Table 1, the ranges of the employed reactant concentration, [Reactant], and the determined k'-k'_0 values are summarized. According to Eq. (E2), the slopes of the k'-k'_0 *versus* [Reactant] plots yield the bimolecular rate coefficients k_i. Nevertheless, the linear relationship between k'-k'_0 and [Reactant] is not always accomplished, as shown in the example in Figure 2. In this figure, a downward curvature in the plot of k'-k'_0 *versus* [CH_3NH_2] was observed at concentrations higher than 3×10^{13} cm^{-3}. As discussed in previous works (Ocaña et al., 2017, 2019; Blázquez et al., 2020; Neeman et al., 2021), this curvature may be the result of the dimerization of the OH-co reactant, CH_3NH_2 in this case. Considering the onset of dimerization, the red straight line in Fig. 2 represents the fit to Eq. (E2) at [CH_3NH_2] below ~3×10^{13} cm^{-3}. In contrast, for reaction R1 the plot of k'-k'_0 *versus* [NH_3] is linear

over the entire concentration range, as displayed in Fig. 3.a. Since this concentration range is much larger than the one for CH_3NH_2 and that the reactivity with OH is significantly slower for NH_3 than for CH_3NH_2, it shows that the dimerization of NH_3 is much less efficient than that of CH_3NH_2 at 22 K. In Figure 3.b., all kinetic data obtained in the linear part of the *k'-k'*$_0$ *versus* [CH_3NH_2] plot are depicted. The bimolecular rate coefficient k_2 at ca. 22 K is, then, obtained from the slope of such a plot.

Reagents. Gases: He (99.999%, Nippon gases), NH_3 (≥99.95%, Merck) and CH_3NH_2 (≥99.0%, Merck) were used as supplied. Aqueous solution of H_2O_2 (Sharlab, initially at 50% w/w) was pre-concentrated as explained earlier (Albaladejo et al., 2003).

Results and discussion

The OH+NH_3 reaction

Temperature dependence of k_1

A summary of the individual rate coefficients k_1 obtained at 22 K and different total pressures of the gas jet is presented in Table 1. Within the stated statistical uncertainties (±2σ), no pressure dependence of k_1 was observed in the investigated range (0.10-0.51 mbar). For this reason, we combined all the kinetic results, as shown in Fig. 3.a. The resulting rate coefficient for the OH+NH_3 reaction at ca. 22 K is:

$$\boldsymbol{k_1(\sim 22\ K) = (2.7 \pm 0.1) \times 10^{-11}\ \ cm^3 s^{-1}}$$

where the uncertainty (±2σ) only includes statistical errors. An additional 10% uncertainty has to be added to account for the systematic errors.

As mentioned in the Introduction section, reaction R1 has been investigated under extensive experimental conditions of temperature (230-2360) K and pressure (1-4000 mbar). A summary of all previous kinetic studies can be found in the most recent investigation from Diau *et al*. (1990). Focusing on the works carried out as a function of temperature (Zellner and Smith, 1974; Hack et al., 1974; Perry et al., 1976; Silver and Kolb, 1980; Fujii et al., 1981, 1986; Salimian et al., 1984; Stephens, 1984; Zabielski and Seery, 1985; Jeffries and Smith, 1986; Diau et al., 1990), a positive temperature dependence of k_1 was observed in all cases, as shown in Figure 4.a. For instance, IUPAC recommends a T-expression for k_1, based on previous results below 450 K (Zellner and Smith, 1974; Perry et al., 1976; Silver and Kolb, 1980; Stephens, 1984; Diau et al., 1990), with an E_a/R factor of 925 K which yields an activation energy (E_a) of 1.8 kcal/mol (Atkinson et al., 2004):

$$\boldsymbol{k_1(230 - 450\ K) = 3.5 \times 10^{-12} exp^{-925\ K/T} \quad cm^3 s^{-1}} \qquad \textbf{(E3)}$$

Even so, as hydrogen atom transfer reactions usually show significant dynamical quantum effects (see Reaction mechanism), the kinetics of reaction R1 deviates from the Arrhenius behavior, showing a curvature in the plot of *ln* k_1 versus 1/*T*. This deviation from Arrhenius behavior has been observed experimentally between 840 and 1425 K (Jeffries and Smith, 1986) and predicted theoretically

between 5 and 4000 K (Espinosa-García and Corchado, 1994; Corchado et al., 1995; Monge-Palacios et al., 2013b; Nguyen and Stanton, 2017; Vahedpour et al., 2018). Most of the computed k_1 have been reported at temperatures higher than 200 K (Espinosa-García and Corchado, 1994; Corchado et al., 1995; Monge-Palacios et al., 2013b; Vahedpour et al., 2018). Only the calculations by Nguyen and Stanton (2017) were performed at lower temperatures and down to 5 K. For ease of presentation, kinetic data between 170 K and 4000 K are plotted in Fig. 4.b in Arrhenius form to clearly show the curvature. Down to 20 K, the predicted k_1 by Nguyen and Stanton (2017), represented by a pink line in Figure 4.c, was 2×10^{-16} cm^3 s^{-1}. This value is around 5 orders of magnitude lower than the experimental result reported in this work. Certainly, further kinetic studies between 230 K and 22 K (and even below) are needed and are planned in our laboratory in the future.

Reaction mechanism

As stated in the Introduction section, the reaction mechanism of the $OH+NH_3$ reaction has been widely studied from a theoretical point of view. The effects of vibrational and translational energy of NH_3 and OH counter partners have been studied by quasi-classical trajectories (Nyman, 1996; Monge-Palacios and Espinosa-Garcia, 2013; Monge-Palacios et al., 2013a) and by quantum scattering calculations (Nyman, 1996). Besides these dynamical studies, *ab initio* calculations based on the transition state theory (TST) were reported. In scheme 1, a simplified illustration of the relative energies to the reactants of the stationary points along the minimum energy pathway (MEP) for the $OH+NH_3$ system is shown. Some studies proposed that product formation in reaction R1 occurs from the transition state and reported energy barriers ranged from 2.03 kcal/mol to 8.94 kcal/mol (Giménez et al., 1992; Bowdridge et al., 1996; Lynch et al., 2000). However, other investigations proposed that reaction R1 occurs through a H-bonded PRC at the entrance channel (Corchado et al., 1995; Bowdridge et al., 1996; Monge-Palacios et al., 2013b; Nguyen and Stanton, 2017). The relative energy of this PRC is positioned a few kcal/mol above the reactants (Nguyen and Stanton, 2017) or -1.8 kcal/mol (Corchado et al., 1995; Monge-Palacios et al., 2013b). In addition to the PRC, a H-bonded complex near the products (PPC, pre-product complex) (Espinosa-García and Corchado, 1994; Corchado et al., 1995; Monge-Palacios et al., 2013b; Nguyen and Stanton, 2017) is proposed at the exit channel, which is stabilized with respect to the reactants by *ca.* -15 kcal/mol. Table 2 summarizes the relative energies of PRC, TS, and PPC from theoretical calculations reported in the literature.

Note that the reaction pathway for the $OH+NH_3$ system is qualitatively similar to the one calculated for the $OH+CH_3OH$ reaction (Ocaña et al., 2019), *i.e.* formation of a H-bonded PRC followed by a transition state with a positive energy barrier. Following that comparison, the observed increase of k_1 can be interpreted by the formation of a long-lived PRC at very low temperatures, which surpasses the energy barrier by quantum mechanical tunnelling.

Effect of k_1 in the abundance of interstellar NH_3

Astrochemical networks apply modified Arrhenius expressions to estimate rate coefficients in a certain temperature interval:

$$\boldsymbol{k(T) = \alpha \left(\frac{T}{300K}\right)^{\beta} exp^{-\gamma/T}} \qquad \textbf{(E4)}$$

For example, KIDA database uses the recommended expression by Atkinson *et al.* (2004) (expression E3, where β=0) and UDfA database uses the following expression:

$$k_1(200-3000\ K) = 1.47\times10^{-13}\left(\frac{T}{300K}\right)^{2.05} exp^{-7\ K/T} \quad cm^3s^{-1} \qquad \textbf{(E5)}$$

Note that these recommended expressions (E3) and (E5) are valid on the stated temperature range. Using these T-expressions to extrapolate rate coefficients down to 22 K is extremely risky. One gets very low values of k_1, on the order of 10^{-27} cm^3 s^{-1} from KIDA expression (E3) and 10^{-16} cm^3 s^{-1} from UDfA (E5), compared with the rate coefficient for the OH+NH_3 reaction determined in the present work. Using Eqs. (E3) and (E5), the rate coefficient at 230 K, k_1(230 K), and extrapolated k_1(200 K) are 6.4 and 8.3×10^{-14} cm^3 s^{-1}, respectively. At the lowest temperature, the k_1(~22 K)/k_1(230 K) ratio is around 380. This value means that the rate of formation of NH_2 radicals from the reaction of NH_3 with OH radicals is really enhanced by more than two orders of magnitude at the typical temperature of a cold dark cloud. Using k_1, obtained in this work, and the rate coefficients from the KIDA and UDfA databases, for a typical cold dark cloud, with H_2 molecular density of 1×10^4 cm^{-3} and a temperature of 10 K (close to the one reproduced in this work) (Agúndez and Wakelam, 2013), the change in modelled abundances of NH_3 is negligible for both reaction networks. The main destruction route for NH_3 in this cold environment is the reaction with H_3O^+ cations, being the reaction of NH_3 with OH radicals around 1% of that with H_3O^+ species.

The OH+CH_3NH_2 reaction

Temperature dependence of k_2

As shown in Table 1, no pressure dependence of the rate coefficient for the OH+CH_3NH_2 reaction was observed in the investigated range. The resulting k_2 at ca. 22 K from the combination of all kinetic data at different gas densities (see Fig. 3.b) is:

$$k_2(\sim22\ \mathrm{K}) = (3.9\pm0.1)\times10^{-10}\ cm^3s^{-1}$$

This value together with previously reported k_2 over the 298-3000 K temperature range (Atkinson et al., 1977; Carl and Crowley, 1998; Tian et al., 2009; Onel et al., 2013; Butkovskaya and Setser, 2016) are depicted in Figure 5. The temperature dependence of k_2 was first measured by Atkinson *et al*. (1977) at T>299 K, who reported the following Arrhenius expression:

$$k_2(299-426\ K) = 1.02\times10^{-11}exp^{(455\pm300)\ cal\ mol^{-1}/RT} \quad cm^3s^{-1} \qquad \textbf{(E6)}$$

The activation energy is slightly negative in this case, -0.45 kcal/mol; however more recently, the negative temperature dependence observed experimentally for reaction R2 was also reported by Onel *et al*. (2013) as an expression with no activation energy and a T-dependent pre-exponential factor (black circles in Fig. 5):

$$k_2(298-500\ K) = 1.89\times10^{-11}\left(\frac{T}{298K}\right)^{-0.56} \quad cm^3s^{-1} \qquad \textbf{(E7)}$$

Using the experimental Onel's expression, the extrapolated k_2(~22 K) is ca. 8×10^{-11} cm^3 s^{-1} (4.9 times lower than the experimental one reported here), while expression (E6) provides an extrapolated k_2(~22 K) of 3.4×10^{-7} cm^3 s^{-1}, which is a non-realistic value for a neutral-neutral reaction. Onel et al. (2013) also computed k_2 between 200 and 500 K (blue line in Fig. 5) to be around 60% higher than the experimental values. No experimental kinetic data have been reported at T>500 K, however Tian *et al.* (2009) predicted a minimum of k_2 around 550 K and a remarkable increase of k_2 at higher

temperatures, *i.e.,* the rate coefficient for the OH+CH_3NH_2 reaction is expected to exhibit a non-Arrhenius behavior. As shown by dashed lines in Fig. 5, the extrapolated k_2 from calculations of Onel *et al.* (2013) is in excellent agreement with our reported value and the value of k_2 obtained by extrapolation of Tian *et al.* (2009) data is only a factor of ca. 2 lower than the experimental value reported in this work. Additional kinetic studies between 298 K and 22 K are clearly needed to confirm the expected trend in the T-dependence of k_2.

Reaction mechanism

The possible exothermic reaction channels for reaction R2 are the H-abstraction from the methyl group (channel R2a) or from the amino group (channel R2b):

$$OH + CH_3NH_2 \rightarrow H_2O + CH_2NH_2 \quad \text{(R2a)}$$

$$\rightarrow H_2O + CH_3NH \quad \text{(R2b)}$$

Theoretically, the mechanism of reaction R2 has been investigated by several groups (Galano and Alvarez-Idaboy, 2008; Tian et al., 2009; Onel et al., 2013; Borduas et al., 2016). The calculations suggest a stepwise mechanism involving the formation of a PRC in the entrance channels (Tian et al., 2009; Onel et al., 2013; Borduas et al., 2016) and a PPC in the exit channels (Tian et al., 2009; Onel et al., 2013). On the other hand, the OH-addition to N and subsequent concerted C-C cleavage, which produces CH_3 radicals and NH_2OH, is endothermic with an energy barrier of 37.4 kcal/mol (Borduas et al., 2016). For that reason, in scheme 2, the energies of the stationary points along the MEP for the OH+CH_3NH_2 reaction is only depicted for the exothermic channels R2a and R2b. In the 299–3000 K temperature range, the dominant exothermic channel is that producing CH_2NH_2 radicals (Galano and Alvarez-Idaboy, 2008; Tian et al., 2009). The branching ratio for R2a (r) at 298 K was reported to be of 0.797 (Galano and Alvarez-Idaboy, 2008) and 0.74 (Tian et al., 2009). In contrast, Borduas *et al*. (2016) concluded that channels R2a and R2b are competitive, with energy barriers close to the entrance level energies of the reactants and within 1 kcal mol^{-1} of each other. Nevertheless, the dominance of R2a channel at room temperature has experimentally been confirmed by Nielsen *et al*. (2011, 2012), Onel *et al*. (2014), and Butkovskaya and Setser (2016). Nielsen *et al*. (2011, 2012) performed experiments in EUPHORE atmospheric chamber providing a r of (0.75 ± 0.05) for channel R2a. A similar value (0.79 ± 0.15) was found by Onel *et al*. (2014) and by Butkovskaya and Setser (2016) (0.74 ± 0.05) No measurements or calculations were found at temperatures below room temperature. Thus, further theoretical and/or experimental studies are needed to know what the branching ratios of channels R2a (forming CH_2NH_2) and R2b (forming CH_3NH) are at interstellar temperatures.

Effect of k_2 in the abundance of interstellar CH_3NH_2

Neither KIDA database nor UDfA network include this OH-reaction as a potential destruction route for CH_3NH_2. However, this reaction is extremely fast at ca. 22 K as it is shown by the experimental rate coefficient for the OH+CH_3NH_2 reaction reported here. Our measured k_2(~22 K) would, then, lead to a quicker depletion of CH_3NH_2 by reaction with OH in astrochemical models. The k_2(~22 K)/k_2(298 K) ratio is around 20, indicating that the use of k_2(298 K) in modelling the ISM would underestimate the loss of CH_3NH_2 by OH by more than one order of magnitude. Using the reported k_2(~22 K) in the pure gas-phase model from Agúndez and Wakelam (2013), the destruction of CH_3NH_2 by OH radicals in a typical cold dark cloud (H_2 molecular density of 1×10^4 cm^{-3} and temperature 10 K) supposes around 1/3 of that initiated by HCO^+ (main depletion route).

Conclusions

The OH-reactivity of NH_3 at ca. 22 K is more than two orders of magnitude higher than that observed at the lowest temperature achieved up to now, 230 K. This confirms that the observed curvature in the Arrhenius plot reflects the increase of k_1 at low temperatures. Further studies are needed to complete the kinetic behavior between 22 K and 230 K and lower temperatures than 22 K. For CH_3NH_2, the determined rate coefficient at ca. 22 K is almost 20 times higher than the one measured at room temperature. The slightly negative temperature dependence of k_2 observed by Atkinson *et al*. (1977) at T>298 K, implies that the OH-reactivity increases at temperatures lower than room temperature, as observed in this work. These new experimental data indicate that the inclusion of the rate coefficient for the OH+NH_3 reaction at 20 K in gas-phase astrochemical models does not significantly change the abundance of NH_3 in a typical cold dark cloud since the main destruction route for NH_3 is the reaction with H_3O^+. However, the inclusion of the rate coefficient for the OH+CH_3NH_2 reaction at 20 K, not considered in KIDA and UDfA networks, indicated that the contribution of this destruction route is not negligible, accounting for 1/3 of the main assumed depletion route (reaction with HCO^+) in this IS environment with temperature close to 10 K.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Author Contributions

D.G. performed the experiments, analyzed the kinetic data, and wrote the draft of the article; B.B. and E.J. contributed to the design and supervision of the experiments; A.C. and E.J. participated in the critical revision of the article; J.A. and E.J. got the funds for carrying out this research and managed the projects. All authors discussed the results and contributed to the final manuscript.

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Tables

Table 1. Summary of the experimental conditions (total gas density (n), jet pressure (p), and reactant concentration in the jet) and corrected *pseudo*-first order rate coefficient ranges.

Reactant	**Laval nozzle**	n**/ 10^{16} cm^{-3}**	p**/ mbar**	**[Reactant]/ 10^{13} cm^{-3}**	k**'-**k**'$_0$/ s^{-1}**	k**(T) / 10^{-11} cm^3 s^{-1}**
NH_3	He23-HP	16.7	0.51	4.2 – 21.6	1932 – 5613	2.7 ± 0.1
	He23-IP	7.4	0.23	3.5 – 10.7	1177 – 2737	2.7 ± 0.1
	He23-LP	3.4	0.10	2.9 – 8.6	408 – 2886	2.9 ± 0.3
CH_3NH_2	He23-HP	16.7	0.51	0.3 – 3.1	589 – 11713	39.2 ± 2.0
	He23-IP	7.4	0.23	0.7 – 3.1	3317 – 11166	36.2 ± 1.4
	He23-LP	3.4	0.10	0.6 – 2.9	2382 – 12034	41.1 ± 1.5

703
704
705 **Table 2.** Summary of the calculated energies relative to reactants (in kcal/mol) of
706 the stationary points in the MEP for the $OH+NH_3$ reaction reported in the literature
707 (see text for more details).
708

PRC	TS	PPC	Products	References
	8.94		-10.69 [(a)]	(Giménez et al., 1992)
	9.05	-15.02	-8.98	Espinosa-García and Corchado (1994)
-1.75	3.65	-17.39	-11.96	Corchado et al. (1995)
	2.03			Bowdridge et al. (1996)
	4.4		-7.1	Lynch et al. (2000)
-1.8	3.3	-15.6	-10.0	Monge-Palacios et al. (2013b)
0.33	2.6	-14.47	-11.49	Nguyen and Stanton (2017)

709 [(a)] From $\Delta H_r^0{}_{298\ K}$

710

711 **Table 3.** Summary of the calculated relative (to reactants) energies (in kcal/mol) of the stationary
712 points in the MEP for the $OH+CH_3NH_2$ reaction reported in the literature (see text for more details).

Channel	PRC	TS	PPC	Products	References
R2a		0.36		-23.19	Galano and Alvarez-Idaboy (2008)
R2b		0.97		-17.00	
R2a	-0.61	-0.52	-28.48	-23.17	Tian et al. (2009)
R2b	-8.45	1.02	-23.03	-17.07	
R2a	-6.38	-1.96	-29.54	-43.52	Onel et al. (2013)
R2b	-6.38	-2.0	-24.19	-26.48	
R2a	-5.4	1.2		-26.0	Borduas et al. (2016)
R2b	-0.2	0.2		-19.0	

713

714

715 **Figure legends**

716 **Scheme 1.** Simplified reaction energy profile along the MEP for the OH + NH_3 reaction.

717

718 **Scheme 2.** Simplified reaction energy profile along the MEP for the OH + CH_3NH_2 reaction.

719

720 **Fig 1.** Examples of the I_{LIF} temporal profile in the presence of similar concentrations of NH_3 (a) and
721 CH_3NH_2 (b) for a total gas density of 7.4×10^{16} cm^{-3}.

722

723 **Fig. 2.** Example of the observed curvature in the bimolecular plots for the OH + CH_3NH_2 reaction at
724 ca. 22 K and 3.4×10^{16} cm^{-3}. Solid line represents k_2 obtained from the fit of all data from Fig. 3.

725

726 **Fig. 3.** Bimolecular plots for the OH-reactions at ca. 22 K with (a) NH_3 and (b) CH_3NH_2.

727

728 **Fig. 4.** (a) Temperature dependence of k_1 (log-log plot) in the 22-4000 K range. Individual rate
729 coefficients at room temperature K (Zellner and Smith, 1974; Perry et al., 1976; Silver and Kolb,
730 1980; Stephens, 1984; Diau et al., 1990) are not included in the figure, but they are considered in the
731 IUPAC recommendation (red curve). (b) Arrhenius plot for k_1 between 170 K and 4000 K to better
732 see the curvature (non-Arrhenius behavior). (c) Extension of the log-log plot shown in (a) to show
733 the great enhancement of k_1 with respect to theoretical predictions at 20 K.

734

735 **Fig. 5.** Temperature dependence of k_2 in the 22-3000 K range.

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