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# Gas-Phase Reactivity of OH Radicals With Ammonia (NH<sub>3</sub>) and Methylamine (CH<sub>3</sub>NH<sub>2</sub>) at Around 22 K

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Interstellar molecules containing N atoms, such as ammonia (NH<sub>3</sub>) and methylamine (CH<sub>3</sub>NH<sub>2</sub>), could be potential precursors of amino acids like the simplest one, glycine (NH<sub>2</sub>CH<sub>2</sub>COOH). 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<sup>16</sup> cm<sup>-3</sup>] in helium. The obtained rate coefficients, with ± 2σ uncertainties, can be included in pure gas-phase or gas-grain astrochemical models to interpret the observed abundances of NH<sub>3</sub> and CH<sub>3</sub>NH<sub>2</sub>. We observed an increase of *k*<sub>1</sub> and *k*<sub>2</sub> with respect to those previously measured by others at the lowest temperatures for which rate coefficients are presently available: 230 and 299 K, respectively. This increase is about 380 times for NH<sub>3</sub> and 20 times for CH<sub>3</sub>NH<sub>2</sub>. Although the OH + NH<sub>3</sub> reaction is included in astrochemical kinetic databases, the recommended temperature dependence for *k*<sub>1</sub> is based on kinetic studies at temperatures above 200 K. However, the OH + CH<sub>3</sub>NH<sub>2</sub> reaction is not included in astrochemical networks. The observed increase in *k*<sub>1</sub> at ca. 22 K does not significantly change the abundance of NH<sub>3</sub> in a typical cold dark interstellar cloud. However, the inclusion of *k*<sub>2</sub> at ca. 22 K, not considered in astrochemical networks, indicates that the contribution of this destruction route for CH<sub>3</sub>NH<sub>2</sub> is not negligible, accounting for 1/3 of the assumed main depletion route (reaction with HCO<sup>+</sup>) in this IS environment.

$$k_1(\text{OH} + \text{NH}_3) = (2.7 \pm 0.1) \times 10^{-11} \text{cm}^3 \text{s}^{-1}$$

$$k_2(\text{OH} + \text{CH}_3\text{NH}_2) = (3.9 \pm 0.1) \times 10^{-10} \text{cm}^3 \text{s}^{-1}$$

**Keywords:** ISM, prebiotic molecules, OH radicals, CRESU technique, reaction kinetics, ultralow temperatures

## 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.,  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , or  $\text{H}_2$ ) (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 ( $\sim 10\text{--}100\text{ K}$ ), such as the so-called dense or dark clouds or pre-stellar cores, range from simple diatomic molecules [e.g.,  $\text{CO}$  or the hydroxyl ( $\text{OH}$ ) radical] to more complex systems (e.g., fullerenes). For instance, the  $\text{OH}$  radical, firstly detected in Cassiopeia A in 1963 (Weinreb et al., 1963), is ubiquitous in the ISM. By definition, carbon-bearing species containing six atoms or more are called complex organic molecules (COMs) (Herbst and van Dishoeck, 2009). Some COMs containing C-O bonds (such as  $\text{CH}_3\text{OH}$ ) and C-N bonds (such as  $\text{CH}_3\text{CN}$ ) can be potential precursors of sugars and amino acids in the presence of water, respectively (Balucani, 2009), under the Earth's conditions. Although ammonia ( $\text{NH}_3$ ) 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  $\text{H}_2$  of  $10^{-8}$  (Wilson et al., 1993) and in TMC-1, with a column density of  $\sim 10^{15}\text{ cm}^{-2}$  (Freeman and Millar, 1983). Another interesting N-bearing species is methylamine ( $\text{CH}_3\text{NH}_2$ ), 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  $\text{H}_2$  for  $\text{CH}_3\text{NH}_2$  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  $\text{NH}_3$  and  $\text{CH}_3\text{NH}_2$  have been proposed as precursors of the simplest amino acid, glycine ( $\text{NH}_2\text{CH}_2\text{COOH}$ ), through H-atom abstraction reactions forming  $\text{NH}_2$  (Sorrell, 2001; Garrod, 2013) and  $\text{CH}_2\text{NH}_2$  radicals, (Woon, 2002; Garrod, 2013); however interstellar glycine remains undetected in the ISM so far.

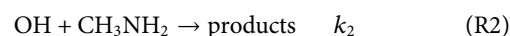
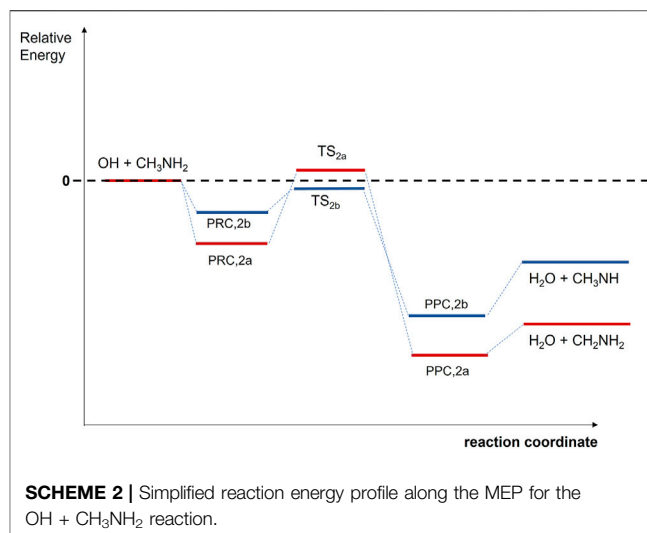
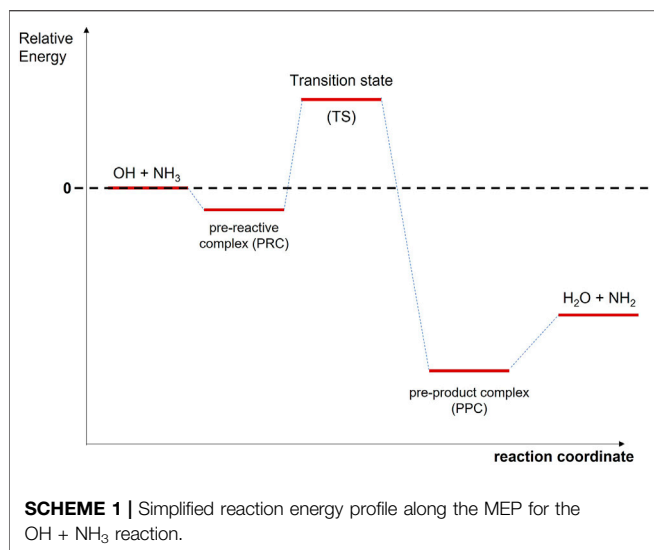
Under the ISM conditions, it has been assumed since a long time (Herbst and Klemperer, 1973) that dissociative

recombination of  $\text{NH}_4^+$  is the main provider of  $\text{NH}_3$  in the gas phase. This cation can be generated through a series of hydrogen abstraction reactions starting from  $\text{N}^+ + \text{H}_2$  leading step by step to  $\text{NH}^+$ ,  $\text{NH}_2^+$ ,  $\text{NH}_3^+$ , and eventually  $\text{NH}_4^+$  (Gerin et al., 2016; Rednyk et al., 2019). Alternatively,  $\text{NH}_2^+$  can be produced by  $\text{H}_3^+ + \text{N}$  (Scott et al., 1997). Although not included in interstellar chemical networks, another potential source of  $\text{NH}_3$  was recently claimed by Gianturco et al. (2019) to be the reaction of the  $\text{NH}_2^-$  anion with  $\text{H}_2$ . Surface reactions have also been proposed as plausible mechanisms to produce ammonia via a series of atomic hydrogen additions to N-hydrides after  $\text{NH}$  has been formed through  $\text{N} + \text{H} \rightarrow \text{NH}$  (Jonusas et al., 2020). Regarding  $\text{CH}_3\text{NH}_2$ , different synthetic routes have been proposed. In the gas-phase, it may be formed via the radiative association between  $\text{NH}_3$  and the methyl radical cation ( $\text{CH}_3^+$ ) followed by dissociative recombination (Herbst, 1985). But  $\text{CH}_3\text{NH}_2$  can also be formed on grain surfaces by sequential hydrogenation of hydrogen cyanide ( $\text{HCN}$ ), as experimentally observed by Theule et al. (2011). Simulations of the irradiation of  $\text{CH}_4$  and  $\text{NH}_3$  ices may also form  $\text{CH}_3\text{NH}_2$  (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  $\text{CH}_3 + \text{NH}_2$  reaction was also suggested as a source of  $\text{CH}_3\text{NH}_2$  during warm-up phases.

It is also important to know how  $\text{NH}_3$  and  $\text{CH}_3\text{NH}_2$  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  $\text{NH}_3$ . e.g., reactions with  $\text{H}$ ,  $\text{CH}$ ,  $\text{CN}$ , among other radicals. Concerning  $\text{CH}_3\text{NH}_2$ , only two depleting reactions by  $\text{CH}$  and  $\text{CH}_3$  radicals are included in KIDA database, while UDFa database does not include any. Until now, the reactivity of  $\text{NH}_3$  with neutral radicals or atoms at ISM temperatures has been investigated experimentally in the presence of  $\text{CN}$  (Sims et al., 1994),  $\text{CH}$  (Bocherel et al., 1996),  $\text{C}_2\text{H}$  (Nizamov and Leone, 2004) and  $\text{C}(^3\text{P})$  (Bourgalais et al., 2015; Hickson et al., 2015) whereas, only the reactivity of  $\text{CH}_3\text{NH}_2$  with  $\text{CN}$  is documented (Sleiman et al., 2018a; 2018b). Due to the important role of  $\text{OH}$  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  $\text{OH}$ -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  $\text{OH} + \text{NH}_3$  reaction (Eq. R1), of interest in atmospheric and combustion chemistry, its gas-phase kinetics has been extensively studied both experimentally and theoretically.



Note that other reaction channels forming  $\text{H}_2\text{NO} + \text{H}_2$ ,  $\text{HNOH} + \text{H}_2$ , or  $\text{H}_2\text{NOH} + \text{H}$  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). Eq. R1 is also of astrochemical interest since it leads to the formation of  $\text{NH}_2$  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 (230–2,360 K) and pressures (1–4,000 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 230–2,360 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 200–4,000 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<sub>3</sub>NH<sub>2</sub> reaction (Eq. 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), 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.

Eq. R2 may proceed by H-abstraction from methyl (–CH<sub>3</sub>) or amino (–NH<sub>2</sub>) groups forming CH<sub>2</sub>NH<sub>2</sub> and CH<sub>3</sub>NH radicals plus water, respectively. The formation of CH<sub>2</sub>NH<sub>2</sub> 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<sub>3</sub> 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<sub>3</sub> and CH<sub>3</sub>NH<sub>2</sub>,  $k_i$  ( $i = 1$  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<sub>3</sub> and CH<sub>3</sub>NH<sub>2</sub> in a typical cold dark interstellar cloud at 10 K.

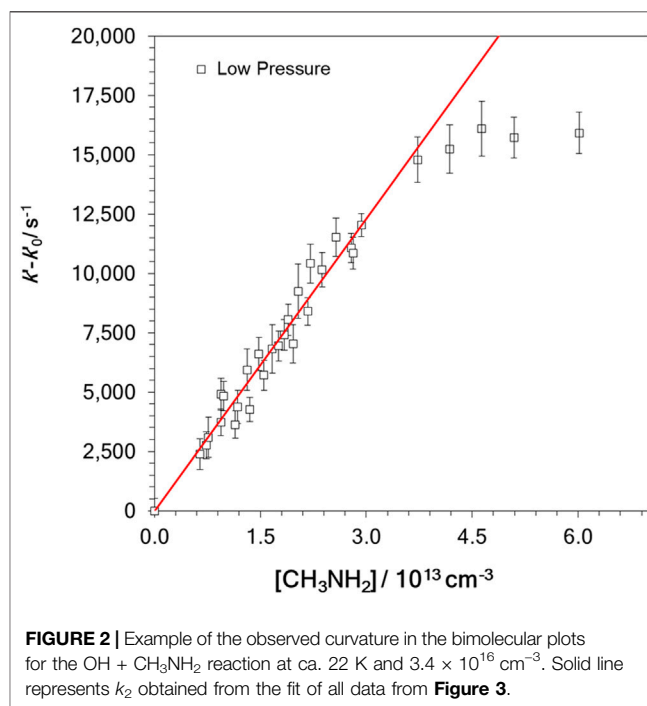
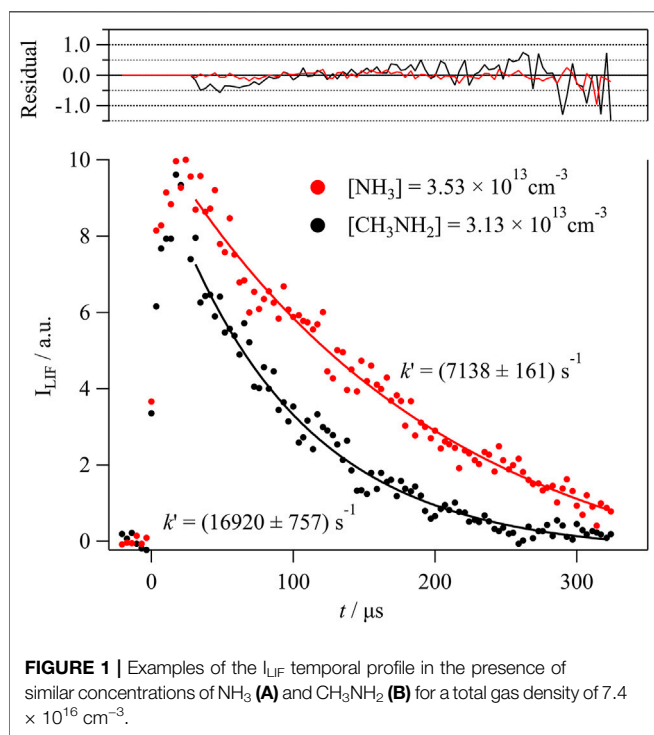
## EXPERIMENTAL METHODS

### 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

**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	$n/10^{16} \text{ cm}^{-3}$	$p/\text{mbar}$	$[\text{Reactant}]/10^{13} \text{ cm}^{-3}$	$k'-k'_0/\text{s}^{-1}$	$k(T)/10^{-11} \text{ cm}^3 \text{ s}^{-1}$
NH <sub>3</sub>	He23-HP	16.7	0.51	4.2–21.6	1932–5613	$2.7 \pm 0.1$
	He23-IP	7.4	0.23	3.5–10.7	1177–2737	$2.7 \pm 0.1$
	He23-LP	3.4	0.10	2.9–8.6	408–2886	$2.9 \pm 0.3$
CH <sub>3</sub> NH <sub>2</sub>	He23-HP	16.7	0.51	0.3–3.1	589–11713	$39.2 \pm 2.0$
	He23-IP	7.4	0.23	0.7–3.1	3317–11166	$36.2 \pm 1.4$
	He23-LP	3.4	0.10	0.6–2.9	2382–12034	$41.1 \pm 1.5$

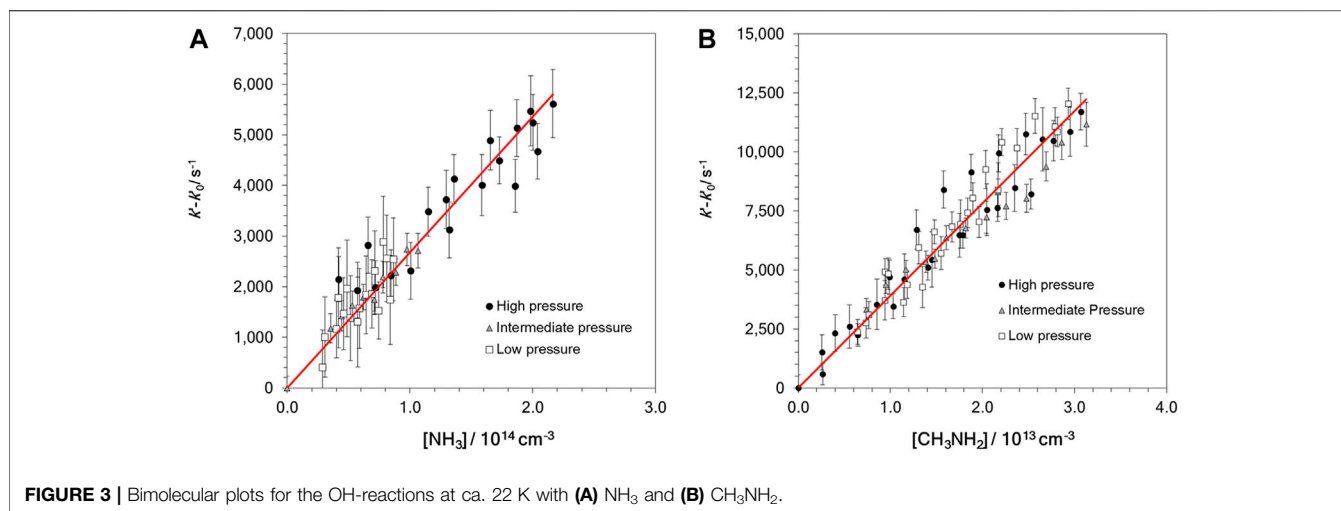


helium as a carrier gas. These nozzles were designed to generate a uniform flow at around 22 K for three different jet pressures (see **Table 1**) (Jiménez et al., 2015; Canosa et al., 2016; Ocaña et al., 2017), thus allowing us to explore the influence of pressure on the reactivity at a constant temperature. Bath gas and reactants (NH<sub>3</sub> or CH<sub>3</sub>NH<sub>2</sub>) 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<sub>3</sub>NH<sub>2</sub> 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  $1.78 \times 10^{-2}$  to  $4.54 \times 10^{-2}$ . In contrast, NH<sub>3</sub> 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<sub>3</sub> ranged from 3 to 15 sccm. The OH-precursor employed was H<sub>2</sub>O<sub>2</sub>, since it is a clean source of OH radicals. Gaseous H<sub>2</sub>O<sub>2</sub> was introduced into the reservoir by bubbling the bath gas through an aqueous solution of H<sub>2</sub>O<sub>2</sub>, as

explained in Jiménez et al. (2005). The flow rate of He through the H<sub>2</sub>O<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> reaction (see *Kinetic Analysis*). The gas mixture formed by He (main flow), He/H<sub>2</sub>O<sub>2</sub>, 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  $(21.7 \pm 1.4)$  K for the He23-HP nozzle,  $(22.5 \pm 0.7)$  K for the He23-IP nozzle, and  $(21.1 \pm 0.6)$  K for the He-23LP nozzle, respectively. Within the fluctuation along the flow axis ( $\pm \sigma$ ), 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<sub>2</sub>O<sub>2</sub>(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





**FIGURE 3** | Bimolecular plots for the OH-reactions at ca. 22 K with (A)  $\text{NH}_3$  and (B)  $\text{CH}_3\text{NH}_2$ .

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 **Figure 1** an example of the temporal evolution of the LIF intensity ( $I_{\text{LIF}}$ ) is presented. As explained in several papers (Jiménez et al., 2015; Ocaña et al., 2018), the observed rise of the  $I_{\text{LIF}}$  signal at  $t > 0$  is due to rotational relaxation of OH, coming from  $\text{H}_2\text{O}_2$  photodissociation, that occurs in a timescale ( $t_0$ ) of less than 30  $\mu\text{s}$  under the conditions of the experiments, especially, at the concentration levels of the reactant, which is an effective quencher. The fit of the recorded  $I_{\text{LIF}}$  profiles to an exponential decay (solid lines in **Figure 1**) confirms that the OH loss follows a pseudo-first order kinetics.

$$I_{\text{LIF}}(t) = I_{\text{LIF}}(t_0) \exp^{-k'(t-t_0)} \quad (\text{E1})$$

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

$$k' = k'_0 + k_i[\text{Reactant}] \quad (\text{E2})$$

where  $k_i$  ( $i = 1$  or  $2$ ) is the bimolecular rate coefficients for OH-reactions with  $\text{NH}_3$  (R1) and  $\text{CH}_3\text{NH}_2$  (R2). In the absence of reactant,  $k'_0$  was measured, and it included the loss of OH radicals by OH-reaction with  $\text{H}_2\text{O}_2$  and other OH losses, such as diffusion out of the detection zone. In **Table 1**, the ranges of the employed reactant concentration,  $[\text{Reactant}]$ , and the determined  $k'-k'_0$  values are summarized. According to **Eq. E2**, the slopes of the  $k'-k'_0$  versus  $[\text{Reactant}]$  plots yield the bimolecular rate coefficients  $k_i$ . Nevertheless, the linear relationship between  $k'-k'_0$  and  $[\text{Reactant}]$  is not always accomplished, as shown in the example in **Figure 2**. In this figure, a downward curvature in the plot of  $k'-k'_0$  vs.  $[\text{CH}_3\text{NH}_2]$  was observed at concentrations higher than  $3 \times 10^{13} \text{ cm}^{-3}$ . 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,  $\text{CH}_3\text{NH}_2$  in this case. Considering the onset of dimerization, the red straight line in **Figure 2** represents the

fit to **Eq. E2** at  $[\text{CH}_3\text{NH}_2]$  below  $\sim 3 \times 10^{13} \text{ cm}^{-3}$ . In contrast, for reaction R1 the plot of  $k'-k'_0$  vs.  $[\text{NH}_3]$  is linear over the entire concentration range, as displayed in **Figure 3A**. Since this concentration range is much larger than the one for  $\text{CH}_3\text{NH}_2$  and that the reactivity with OH is significantly slower for  $\text{NH}_3$  than for  $\text{CH}_3\text{NH}_2$ , it shows that the dimerization of  $\text{NH}_3$  is much less efficient than that of  $\text{CH}_3\text{NH}_2$  at 22 K. In **Figure 3B**, all kinetic data obtained in the linear part of the  $k'-k'_0$  vs.  $[\text{CH}_3\text{NH}_2]$  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),  $\text{NH}_3$  ( $\geq 99.95\%$ , Merck) and  $\text{CH}_3\text{NH}_2$  ( $\geq 99.0\%$ , Merck) were used as supplied. Aqueous solution of  $\text{H}_2\text{O}_2$  (Sharlab, initially at 50% w/w) was pre-concentrated as explained earlier (Albaladejo et al., 2003).

## RESULTS AND DISCUSSION

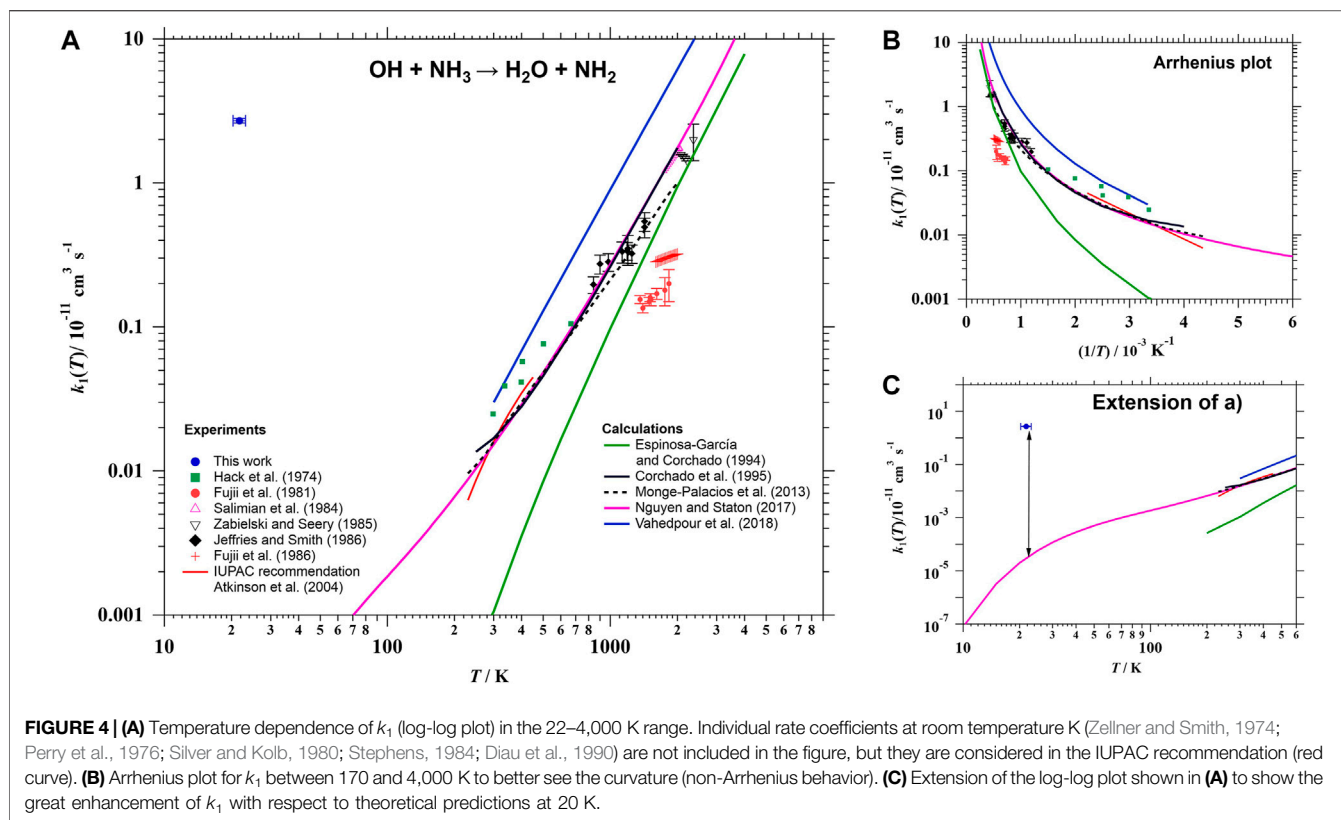
### The OH + $\text{NH}_3$ Reaction Temperature Dependence of $k_1$

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 ( $\pm 2\sigma$ ), 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 **Figure 3A**. The resulting rate coefficient for the OH +  $\text{NH}_3$  reaction at ca. 22 K is:

$$k_1 (\sim 22 \text{ K}) = (2.27 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

where the uncertainty ( $\pm 2\sigma$ ) only includes statistical errors. An additional 10% uncertainty has to be added to account for the systematic errors.

As mentioned in the Introduction section, **Eq. R1** has been investigated under extensive experimental conditions of temperature (230–2,360 K) and pressure (1–4,000 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 4A**. 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):

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

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 1,425 K (Jeffries and Smith, 1986) and predicted theoretically between 5 and 4,000 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 and

4,000 K are plotted in **Figure 4B** 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 4C**, was  $2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ . This value is around five orders of magnitude lower than the experimental result reported in this work. Certainly, further kinetic studies between 230 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<sub>3</sub> reaction has been widely studied from a theoretical point of view. The effects of vibrational and translational energy of NH<sub>3</sub> and OH counter partners have been studied by quasi-classical trajectories (Nyman, 1996; Monge-Palacios and Espinosa-García, 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<sub>3</sub> 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.,

**TABLE 2** | Summary of the calculated energies relative to reactants (in kcal/mol) of the stationary points in the MEP for the OH + NH<sub>3</sub> reaction reported in the literature (see text for more details).

PRC	TS	PPC	Products	References
-1.75	8.94	—	-10.69 <sup>a</sup>	Giménez et al. (1992)
	9.05	-15.02	-8.98	Espinosa-García and Corchado (1994)
	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)

<sup>a</sup>From  $\Delta H_{298}^{\circ}$  K.

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<sub>3</sub> system is qualitatively similar to the one calculated for the OH + CH<sub>3</sub>OH 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<sub>3</sub>

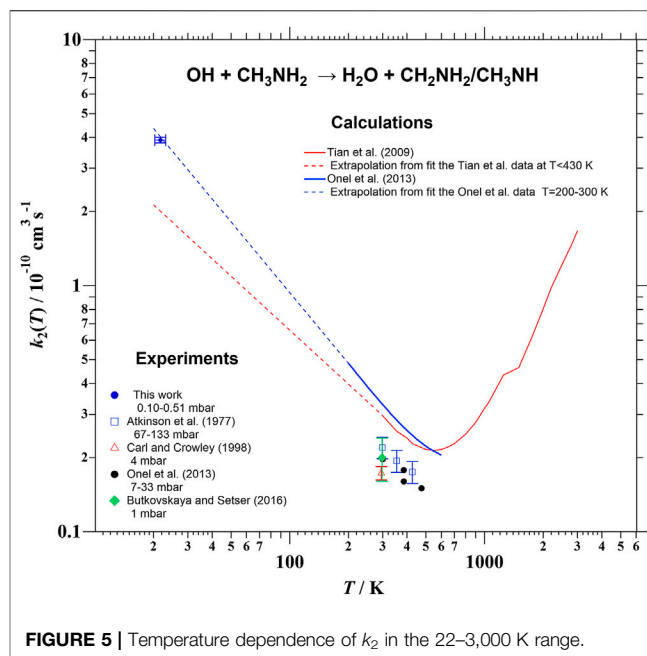
Astrochemical networks apply modified Arrhenius expressions to estimate rate coefficients in a certain temperature interval:

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

For example, KIDA database uses the recommended expression by Atkinson et al. (2004) (Eq. E3, where  $\beta = 0$ ) and UfA database uses the following expression:

$$k_1(200 - 3,000\text{K}) = 1.47 \times 10^{-13} \left( \frac{T}{300\text{K}} \right)^{2.05} \exp^{-7\text{K}/T} \text{cm}^3 \text{s}^{-1} \quad (\text{E5})$$

Note that these recommended Eqs E3, 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  $10^{-27} \text{cm}^3 \text{s}^{-1}$  from KIDA expression Eq. E3 and  $10^{-16} \text{cm}^3 \text{s}^{-1}$  from UfA Eq. E5, compared with the rate coefficient for the OH + NH<sub>3</sub> reaction determined in the present work. Using Eqs E3 and E5, the rate coefficient at 230 K,  $k_1(230 \text{K})$ , and extrapolated  $k_1(200 \text{K})$  are 6.4 and  $8.3 \times 10^{-14} \text{cm}^3 \text{s}^{-1}$ , respectively. At the lowest temperature, the  $k_1(\sim 22 \text{K})/k_1(230 \text{K})$  ratio is around 380. This value means that



**FIGURE 5** | Temperature dependence of  $k_2$  in the 22–3,000 K range.

the rate of formation of NH<sub>2</sub> radicals from the reaction of NH<sub>3</sub> 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 UfA databases, for a typical cold dark cloud, with H<sub>2</sub> molecular density of  $1 \times 10^4 \text{cm}^{-3}$  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<sub>3</sub> is negligible for both reaction networks. The main destruction route for NH<sub>3</sub> in this cold environment is the reaction with H<sub>3</sub>O<sup>+</sup> cations, being the reaction of NH<sub>3</sub> with OH radicals around 1% of that with H<sub>3</sub>O<sup>+</sup> species.

### The OH + CH<sub>3</sub>NH<sub>2</sub> Reaction Temperature Dependence of $k_2$

As shown in **Table 1**, no pressure dependence of the rate coefficient for the OH + CH<sub>3</sub>NH<sub>2</sub> 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 **Figure 3B**) is:

$$k_2(\sim 22\text{K}) = (3.9 \pm 0.1) \times 10^{-10} \text{cm}^3 \text{s}^{-1}$$

This value together with previously reported  $k_2$  over the 298–3,000 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  $T > 299 \text{K}$ , who reported the following Arrhenius expression:

$$k_2(299 - 426 \text{K}) = 1.02 \times 10^{-11} \exp^{(455 \pm 300) \text{cal mol}^{-1}/RT} \text{cm}^3 \text{s}^{-1} \quad (\text{E6})$$

The activation energy is slightly negative in this case, -0.45 kcal/mol; however more recently, the negative temperature dependence observed experimentally for Eq. R2 was also reported by Onel et al. (2013) as an expression with



**TABLE 3** | Summary of the calculated relative (to reactants) energies (in kcal/mol) of the stationary points in the MEP for the OH + CH<sub>3</sub>NH<sub>2</sub> 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	

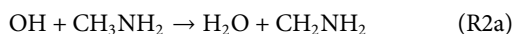
no activation energy and a T-dependent pre-exponential factor (black circles in **Figure 5**):

$$k_2(298 - 500\text{K}) = 1.89 \times 10^{-11} \left( \frac{T}{298\text{K}} \right)^{-0.56} \text{cm}^3 \text{s}^{-1} \quad (\text{E7})$$

Using the experimental Onel's expression, the extrapolated  $k_2(\sim 22\text{K})$  is ca.  $8 \times 10^{-11} \text{cm}^3 \text{s}^{-1}$  (4.9 times lower than the experimental one reported here), while **Eq. E6** provides an extrapolated  $k_2(\sim 22\text{K})$  of  $3.4 \times 10^{-7} \text{cm}^3 \text{s}^{-1}$ , 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 **Figure 5**) to be around 60% higher than the experimental values. No experimental kinetic data have been reported at  $T > 500\text{K}$ , 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<sub>3</sub>NH<sub>2</sub> reaction is expected to exhibit a non-Arrhenius behavior. As shown by dashed lines in **Figure 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 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 **Eq. R2** are the H-abstraction from the methyl group (**Eq. R2a**) or from the amino group (**Eq. R2b**):



Theoretically, the mechanism of **Eq. 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<sub>3</sub> radicals and NH<sub>2</sub>OH, 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<sub>3</sub>NH<sub>2</sub> reaction is only depicted for the exothermic channels R2a and R2b. The relative energies of PRC, TS, and PPC for reaction pathways R2a and R2b

reported in theoretical calculations are summarized in **Table 3** (Galano and Alvarez-Idaboy, 2008; Tian et al., 2009; Onel et al., 2013; Borduas et al., 2016). In the 299–3,000 K temperature range, the dominant exothermic channel is that producing CH<sub>2</sub>NH<sub>2</sub> 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<sup>-1</sup> 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), Butkovskaya and Setser (2016). Nielsen et al. (2011, 2012) performed experiments in EUPHORE atmospheric chamber providing a  $r$  of  $(0.75 \pm 0.05)$  for channel R2a. A similar value  $(0.79 \pm 0.15)$  was found by Onel et al. (2014) and by Butkovskaya and Setser (2016)  $(0.74 \pm 0.05)$ . 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<sub>2</sub>NH<sub>2</sub>) and R2b (forming CH<sub>3</sub>NH) are at interstellar temperatures.

## Effect of $k_2$ in the Abundance of Interstellar CH<sub>3</sub>NH<sub>2</sub>

Neither KIDA database nor UDFa network include this OH-reaction as a potential destruction route for CH<sub>3</sub>NH<sub>2</sub>. However, this reaction is extremely fast at ca. 22 K as it is shown by the experimental rate coefficient for the OH + CH<sub>3</sub>NH<sub>2</sub> reaction reported here. Our measured  $k_2(\sim 22\text{K})$  would, then, lead to a quicker depletion of CH<sub>3</sub>NH<sub>2</sub> by reaction with OH in astrochemical models. The  $k_2(\sim 22\text{K})/k_2(298\text{K})$  ratio is around 20, indicating that the use of  $k_2(298\text{K})$  in modelling the ISM would underestimate the loss of CH<sub>3</sub>NH<sub>2</sub> by OH by more than one order of magnitude. Using the reported  $k_2(\sim 22\text{K})$  in the pure gas-phase model from Agúndez and Wakelam (2013), the destruction of CH<sub>3</sub>NH<sub>2</sub> by OH radicals in a typical cold dark cloud (H<sub>2</sub> molecular density of  $1 \times 10^4 \text{cm}^{-3}$  and temperature 10 K) supposes around 1/3 of that initiated by HCO<sup>+</sup> (main depletion route).

## CONCLUSION

The OH-reactivity of NH<sub>3</sub> 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 and 230 K and lower temperatures than 22 K. For  $\text{CH}_3\text{NH}_2$ , 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 +  $\text{NH}_3$  reaction at 20 K in gas-phase astrochemical models does not significantly change the abundance of  $\text{NH}_3$  in a typical cold dark cloud since the main destruction route for  $\text{NH}_3$  is the reaction with  $\text{H}_3\text{O}^+$ . However, the inclusion of the rate coefficient for the OH +  $\text{CH}_3\text{NH}_2$  reaction at 20 K, not considered in KIDA and UfA networks, indicated that the contribution of this destruction route is not negligible, accounting for 1/3 of the main assumed depletion route (reaction with  $\text{HCO}^+$ ) in this IS environment with temperature close to 10 K.

## DATA AVAILABILITY STATEMENT

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

## AUTHOR CONTRIBUTIONS

DG performed the experiments, analyzed the kinetic data, and wrote the draft of the article; BB and EJ contributed to the

design and supervision of the experiments; AC and EJ participated in the critical revision of the article; JA and EJ 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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