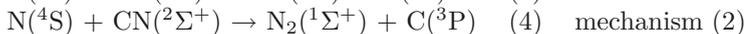# INTERSTELLAR CHEMISTRY OF ATOMIC NITROGEN: LOW TEMPERATURE KINETICS OF THE N + OH, N + CN AND N + NO REACTIONS

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Abstract. More than 100 reactions between stable molecules and free radicals have been shown to remain rapid at low temperatures. In contrast, reactions between two unstable radicals have received much less attention due to the added complexity of producing and measuring excess radical concentrations. We performed kinetic experiments on the barrierless N + OH and N + CN reactions in a supersonic flow (Laval nozzle) reactor. The results provide insight into the gas-phase formation mechanisms of molecular nitrogen in interstellar clouds (ISCs).

1 Introduction

The chemistry of low temperature environments, such as ISCs, was thought to be governed by reactions involving electrically charged species (Herbst *et al.* 1994) until recent advances in experimental and theoretical methods showed that reactions between neutral species could occur and even dominate in some low temperatures regions. In contrast to atomic carbon and oxygen, nitrogen cannot react with H_3^+ in dark clouds to form NH^+ or NH_2^+ because the channel forming NH^+ is endothermic and there is no low energy path to form NH_2^+ (Milligan *et al.* 2000). Instead, atomic nitrogen reacts with neutral species in the following reactions which mediate its transformation to molecular nitrogen (N_2):
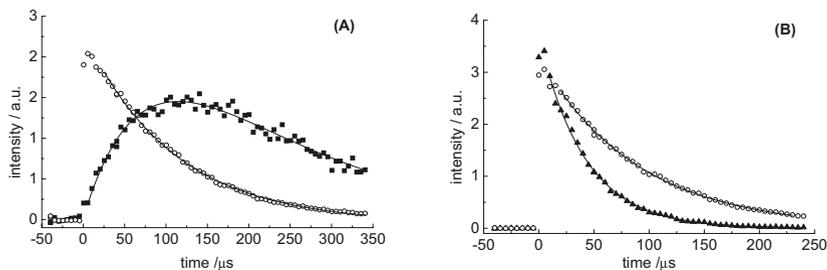
$N(^4S) + OH(^2\Pi) \rightarrow NO(^2\Pi) + H(^2S)$ (1)
$N(^4S) + NO(^2\Pi) \rightarrow N_2(^1\Sigma^+) + O(^3P)$ (2)   mechanism (1)
$N(^4S) + CH(^2\Pi) \rightarrow CN(^2\Pi) + H(^2S)$ (3)
$N(^4S) + CN(^2\Sigma^+) \rightarrow N_2(^1\Sigma^+) + C(^3P)$ (4)   mechanism (2)

Subsequent reactions of N_2 form N_2H^+ and NH_3 which are used as tracers of molecular density.

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Fig. 1. (A) Typical decays obtained at 148 K for the N+OH reaction: solid squares, NO; open circles, OH. (B) Typical decays obtained at 296 K for the N+CN reaction: solid triangles, CN; open circles, OH.

The CRESU (Cinétique de Réaction en Écoulement Supersonique Uniforme) technique (Sims *et al.* 1992) applies Laval nozzle expansions to cool gases isentropically whilst avoiding the wall loss effects incurred in conventional cryogenic systems. This method has been used to measure the rates for numerous reactions between neutral species at temperatures as low as 6 K (Berteloite *et al.* 2010), although only one of them, the O + OH reaction was between two unstable radicals (Carty *et al.* 2006). Nevertheless, the atomic oxygen production and detection scheme used in this study cannot be used to study the reactions of other atomic species such as N or H with radicals. Several challenges face experimentalists studying radical-radical kinetics. First, sufficiently large quantities of one of the radical species must be generated such that its concentration satisfies the requirement for pseudo-first-order kinetics. Second, this excess reagent concentration must be quantified to extract the thermal rate constant. Finally, the method must be general, so that it can be applied universally to investigate an extensive range of radical-radical reactions.

2   Experiment

Experiments were performed using a continuous CRESU apparatus, the main features of which have been previously described (Daranlot *et al.* 2011). Briefly, four Laval nozzles based on Ar and N_2 as the carrier gases were used to perform kinetic measurements at specified temperatures between 56 and 172 K and measurements at 296 K were performed without a nozzle. OH and CN radicals were generated by pulsed photodissociation of H_2O_2 and ICN respectively at 266 nm directly in the supersonic flow. Ground-state atomic nitrogen was generated upstream of the Laval nozzle by microwave discharge. We did not measure the atomic nitrogen concentration directly. Instead, we used an established technique, the relative rate method to measure the unknown rate of the target reaction relative to the known rate of a reference reaction; the two reactions sharing a common excess reagent species (atomic nitrogen in this case). The ratio of the pseudo-first-order losses of the two minor reagent species yields the ratio of the rate constants for these reactions. For the study of reaction (1), product NO reacts with excess atomic
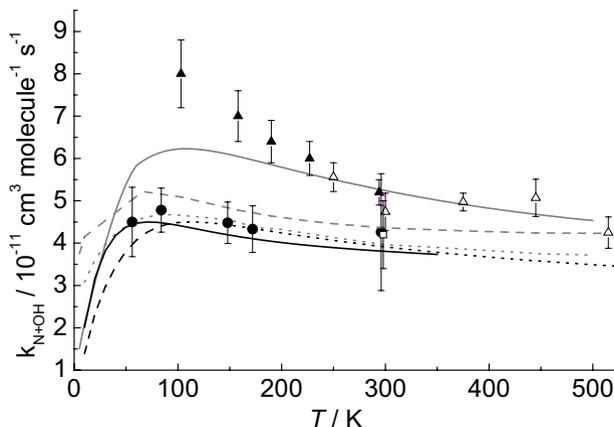
Fig. 2. Rate constants for the N+OH reaction as a function of temperature. Experimental values: solid triangles, Smith & Stewart (1994); open triangles, Howard & Smith (1981); open square Brune *et al.* (1983); solid circles, this work (Daranlot *et al.* 2011). Theoretical values: gray dashed line, Edvardsson *et al.* (2006); gray dotted line, Jorfi *et al.* (2009); black dotted line, Li *et al.* (2011); gray solid line Ge *et al.* (2008); black lines, Daranlot *et al.* (2011): approximate (dash) and exact (solid) QM calculations.

nitrogen (reaction (2)) which can thus serve as the reference process as the rate constants are already known (Bergeat *et al.* 2009). OH and NO were followed simultaneously by laser-induced fluorescence (Fig. 1A). The pseudo-first-order rate constants k_1' and k_2' are determined by fits to temporal profiles as explained in Daranlot *et al.* (2011). For the study of reaction (4), OH and CN are created simultaneously in the supersonic flow. In this case, reaction (1) is used as the reference process and the OH and CN fluorescence intensities are followed as a function of time (Fig. 1B). Both signals can be fitted by a single exponential decay providing the pseudo-first-order rate constants k_1' and k_4' for a given flow of N_2 through the microwave discharge. Potential secondary processes are systematically verified and therefore should not skew the measured rate constants.

3 Results and astrophysical implications

The pseudo-first-order rate constants are plotted against the corresponding rate constants for the reference reaction to yield the ratios k_1/k_2 and k_4/k_1 from the slope. We have performed the only measurements to date of the N + OH reaction below 100 K (Daranlot *et al.* 2011): Experimental values of k_1 are obtained by multiplying the ratio k_1/k_2 by k_2 (Bergeat *et al.* 2009). The results of N + OH are shown in Figure 2 alongside previous experimental studies and theoretical calculations. The most recent measurements of the N + OH reaction (Smith & Stewart 1994) between 103 and 294 K predicted a strong negative temperature dependence. Recent calculations (Edvardsson *et al.* 2006; Ge *et al.* 2008; Jorfi & Honvault 2009) show that the reaction could be slower than predicted by

Smith & Stewart (1994) with a much less pronounced temperature dependence. The experimental and theoretical rate constants determined in this study agree with previous calculations, showing that earlier experimental measurements may have overestimated the rate constant for reaction (1). Measurements at room temperature for the N + CN reaction are in excellent agreement with previous results (Whyte & Phillips 1983; Atakan *et al.* 1992). Measurements below room temperature were also performed (Daranlot *et al.* 2012).

Current chemical models indicate that elemental nitrogen should be mostly present in dark clouds as N_2. Nevertheless, indirect observations suggest that this is not the case. To bring results more in line with observations, some models use depleted initial concentrations of important species or artificially lower the rate constants for important reactions. The excellent agreement between recent theoretical results and experimental measurements presented here for the N + OH reaction validates our experimental method and should permit the measurement of rate constants for a wide range of atom-radical reactions in the near future. We show that reactions involved in the transformation of atomic nitrogen to N_2 are slower than predicted. The low observed fractional abundances of NO and N_2 in prestellar cores might be explained by a combination of physical and chemical processes.

References

Atakan, B., Kocis, D., Wolfrum, J., & Nelson, P., 1992, Symp. (Int.) on Combust., 24, 691

Bergeat, A., Hickson, K.M., Daugey, N., Caubet, P., & Costes, M., 2009, Phys. Chem. Chem. Phys., 11, 8149

Berteloite, C., Lara, M., Bergeat, A., *et al.*, 2010, Phys. Rev. Lett., 105, 203201

Brune, W.H., Schwab, J.J., & Anderson, J.G., 1983, J. Phys. Chem., 87, 4503

Carty, D., Goddard, A., Kohler, S.P.K., Sims, I.R., & Smith, I.W.M., 2006, J. Phys. Chem. A, 110, 3101

Daranlot, J., Jorfi, M., Xie, C., *et al.*, 2011, Science, 334, 1538

Daranlot, J., Hincelin, U., Bergeat, A., *et al.*, 2012, Proc. Natl. Acad. Sci. USA, 109, 10233

Edvardsson, D., Williams, C.F., & Clary, D.C., 2006, Chem. Phys. Lett., 431, 261

Ge, M.H., Chu, T.S., & Han, K.L., 2008, J. Theo. Comput. Chem., 7, 607

Herbst, E., Lee, H.-H., Howe, D.A., & Millar, T.J., 1994, MNRAS, 268, 335

Howard, M.J., & Smith, I.W.M., 1981, J. Chem. Soc. Faraday Trans., 2, 77, 997

Jorfi, M., Honvault, P., & Halvick, P., 2009, Chem. Phys. Lett., 471, 65

Li, A., Xie, C., Xie, D., & Guo, H., 2011, J. Chem. Phys., 134, 194309

Maret, S., Bergin, E.A., & Lada, C.J., 2006, Nature, 442, 425

Milligan, D.B., Fairley, D.A., Freeman, C.G., & McEwan, M.J., 2000, Int. J. Mass Spectrom., 202, 351

Sims, I.R., Queffelec, J.L., Defrance, A., *et al.*, 1992, J. Chem. Phys., 97, 8798

Smith, I.W.M., & Stewart, D.W.A., 1994, J. Chem. Soc. Faraday Trans., 90, 3221

Whyte, A.R., & Phillips, L.F., 1983, Chem. Phys. Lett., 98, 590