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KINETIC STUDIES ON LOW-TEMPERATURE SOLID-STATE REACTIONS IN INTERSTELLAR ICES

P. Theulé¹, F. Duvernay¹, F. Mispelaer¹, J.B. Bossa¹, F. Borget¹,
G. Danger¹ and T. Chiavassa¹

Abstract. Understanding the chemistry of the interstellar medium necessitates the use of gas-grain chemistry codes along with extensive databases of gas-phase and solid-phase reactions. If reaction rates have been measured for various types of gas phase reactions, no experimental kinetic studies are available for determining solid-state thermal reaction rates. We present here an experimental kinetic study of few purely thermal low-temperature solid-state reactions relevant to interstellar ice chemistry.

1 Introduction

Many chemical reactions are taking place on and in the interstellar ice mantle. Among them, many reactions are purely thermal, such as reactions involving small molecules: H_2CO , NH_3 , CO_2 , HNCO , or HCN . We will show how it is possible to measure the kinetics of these reactions and to derive kinetic parameters, which are extremely useful to gas-grain models. Kinetic experiments were performed on the RING experimental set-up (Bossa *et al.* 2009). We will take the formation of the OCN^- anion from the acid base reactions $\text{NH}_3 + \text{HNCO}$ and $\text{H}_2\text{O} + \text{HNCO}$ as examples and we will show how it is possible to extend such kinetic studies to other reactions. The strong absorption feature at $4.62\ \mu\text{m}$ ($2165\ \text{cm}^{-1}$) is commonly attributed to the solid-phase cyanate ion OCN^- (Grim & Greenberg 1987; Lowenthal *et al.* 2000; Novozamsky *et al.* 2001; Soifer *et al.* 1979). Although absent in starless dark molecular clouds (Knez *et al.* 2005), this feature appears in the spectra of several protostellar objects with large source-to-source abundance variations (van Broekhuizen *et al.* 2005). The kinetic of the formation of solid-state OCN^- can allow us to correlate the OCN^- band intensity to the time evolution

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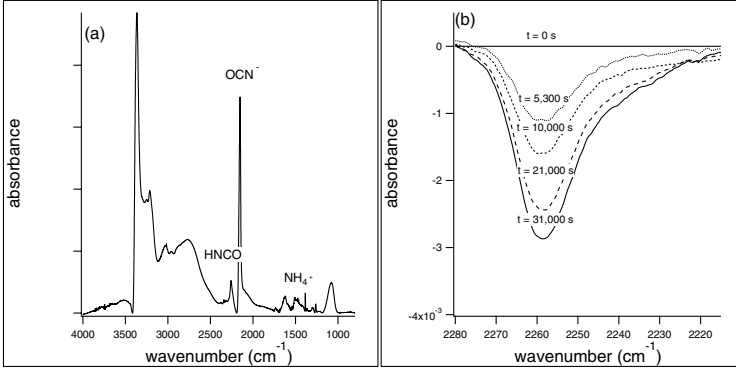


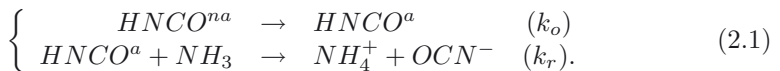
Fig. 1. (a) Infrared spectrum of an HNCO:NH₃ ice mixture in a 1:20 ratio. OCN[−] has a band at 2151 cm^{−1}. HNCO has a band at 2259 cm^{−1} corresponding to HNCO in a NH₃ environment. (b) Difference spectrum with respect to $t = 0$ s of the HNCO 2259 cm^{−1} band at $T = 15$ K at $t = 5\,300$ s, $10\,000$ s, $21\,000$ s, and $31\,000$ s.

of protostellar objects. The kinetic formalism usually used for reactions in the liquid-phase seems to be directly transposable to reactions occurring in the solid phase such as NH₃+H₂CO (Bossa *et al.* 2009) or NH₃+CO₂.

2 Kinetics of the HNCO + NH₃ reaction

The more straightforward way to obtain OCN[−] is from the HNCO + NH₃ → NH₄⁺ + OCN[−] acid-base reaction (Raunier *et al.* 2003). After deposition the HNCO:NH₃ ice mixture is warmed to a fixed temperature. This defines the initial time ($t = 0$ s) of the kinetic experiment. When the temperature is kept to this fixed value, the OCN[−] band at 2151 cm^{−1} and the NH₄⁺ band at 1495 cm^{−1} are progressively growing, while the bands corresponding to HNCO and NH₃ are decreasing along with time. Figure 1 shows the time evolution of the IR spectrum of a HNCO:NH₃ ice mixture in a 1:20 ratio at a fixed 15 K temperature. Figure 2 shows the decrease of the HNCO normalized column density along with time, as derived from its integrated band at 2259 cm^{−1}, at a fixed $T = 20$ K temperature.

To explain the biexponential decay curve shape and that the reaction yield is not 100%, we break down the HNCO decay into two processes: a fast process and a slow process. The fast process corresponds to a low activation barrier chemical reaction and has a rate constant k_r . The slow process, rate constant k_o , consists of HNCO rotating around its center of mass within its NH₃ environment, to achieve a configuration state, noted HNCO^a, which corresponds to the configuration enabling the chemical reaction. This two-consecutive-step model is expressed in Equation (2.1):



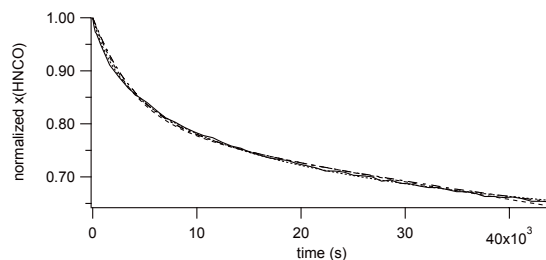


Fig. 2. Time evolution of the normalized HNCO molar fraction recorded by FTIR spectroscopy (full line) at $T = 20$ K for a HNCO:NH₃ mixture where NH₃ is largely in excess (1:20 concentration ratio). Fitting the experimental data against the analytical expressions for the HNCO time evolution using a rate equation approach (dashed line), gives the value for the reaction rate at a fixed temperature.

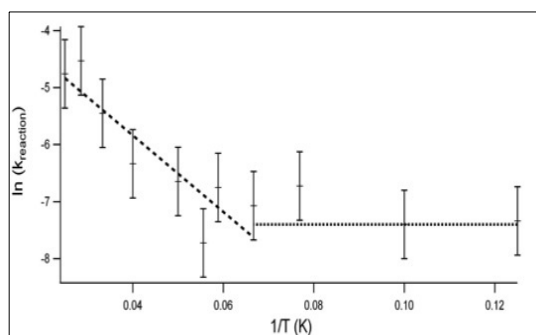


Fig. 3. $\ln(k_r)$ as a function of the inverse of the temperature. k_r is the rate for the HNCO + NH₃ $\rightarrow$ NH₄⁺ + OCN⁻ reaction using a rate equation approach. The uncertainty on a point is given by the dispersion of the measurements at 20 K. The dashed lines represent the fit of the experimental points against an Arrhenius law for each approach.

We then can write the kinetic equations for the two consecutive phenomena as two consecutive first-order reactions:

$$\begin{cases} \frac{dx(\text{HNCO}^{na})}{dt} &= -k_o(T) \times x(\text{HNCO}^{na}) \\ \frac{dx(\text{HNCO}^a)}{dt} &= k_o(T) \times x(\text{HNCO}^{na}) - k_r(T) \times x(\text{HNCO}^a). \end{cases} \quad (2.2)$$

Fitting the experimental data to this set of equations provides us values of k_o and k_r for different fixed temperatures. We carried out such isothermal experiments at different fixed temperatures to measure formation rates of NH₄⁺OCN⁻ from the HNCO + NH₃ reaction. The temperature dependency of k_r is reported in Figure 3.

Figure 3 shows that $k_r(T)$ has two temperature domains. In the first domain, between 60 K and 15 K, the reaction rate can be fitted against an Arrhenius law $k(T) = \nu_r \times \exp \frac{-E_r}{RT}$. We found an activation energy $E_r = 0.4 \pm 0.1$ kJ mol⁻¹

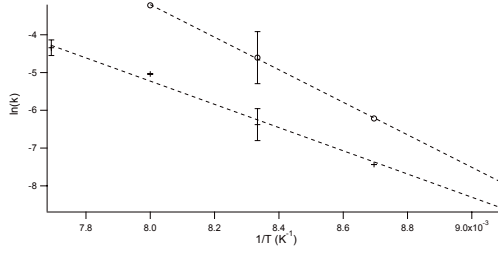


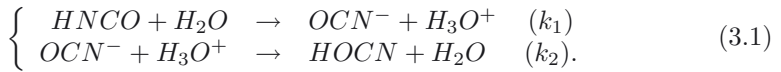
Fig. 4. $\ln(k_1)$ (crosses) and $\ln(k_2)$ (circles) as a function of the inverse of the temperature, k_1 and k_2 being the rates for the $\text{HNCO} + \text{H}_2\text{O} \rightarrow \text{OCN}^- + \text{H}_3\text{O}^+$ and the $\text{OCN}^- + \text{H}_3\text{O}^+ \rightarrow \text{HO CN} + \text{H}_2\text{O}$ reactions respectively. The uncertainty on a point is given by the dispersion of the measurements for the same temperature around the averaged value. The dashed lines represent the fit of the experimental points against an Arrhenius law.

(48 ± 12 K) and a pre-exponential factor $\nu_r = 0.0035 \pm 0.0015 \text{ s}^{-1}$ for the reaction between 60 K and 15 K. In the second domain between 15 K and 8 K, the reaction rate levels off, and the temperature dependence shows a plateau. The plateau can be interpreted as caused by a quantum tunneling reaction. This quantum tunneling regime coexists with the thermal regime, but becomes predominant at low-temperature when the thermally induced reaction becomes minor.

A fit with an Arrhenius law ($k(T) = \nu \times \exp \frac{-E}{RT}$), of the experimental rate constants gives a small activation barrier, $E_r = 0.4 \pm 0.1 \text{ kJ mol}^{-1}$ (48 ± 12 K) (Theule *et al.* 2011b) as seen in Figure 3.

3 Kinetics of the $\text{HNCO} + \text{H}_2\text{O}$ reaction

The same formalism can be applied to the $\text{HNCO} + \text{H}_2\text{O}$ system:



This set of two reactions allows the isomerization of HNCO into HO CN on a water ice surface. Following the same experimental protocol and the same kinetic equations formalism we can derive the temperature dependence of the two corresponding rate constants as seen in Figure 4.

Fitting the experimental rates with an Arrhenius equation gives the activation energies for both reactions. As for the $\text{OCN}^- + \text{H}_3\text{O}^+ \rightarrow \text{HO CN} + \text{H}_2\text{O}$ reaction, we find an activation energy $E_2 = 36 \pm 1 \text{ kJ mol}^{-1}$, and a pre-exponential factor of $\nu_2 = 4_{-2}^{+4} 10^{13} \text{ s}^{-1}$. Accordingly we can write the reaction rate for the $\text{OCN}^- + \text{H}_3\text{O}^+ \rightarrow \text{HO CN} + \text{H}_2\text{O}$ reaction as $k_2(T) = 4 \cdot 10^{13} \exp \frac{-36 \pm 1 \text{ kJ mol}^{-1}}{RT} \text{ s}^{-1}$.

4 Conclusion

We have shown that it is possible to measure experimentally solid-state reaction rates on interstellar ice analogs. These measured reaction rates are extremely useful to gas-grain chemistry codes as they provide the dynamics of bulk reactions within interstellar ice mantle. The technique is simple to apply and should be used to measure. For example we have shown that it was possible to use this kinetic approach to the $\text{NH}_3 + \text{H}_2\text{CO} \rightarrow \text{NH}_2\text{CH}_2\text{OH}$ reactions (Bossa *et al.* 2009). This work should be pursued and extended to other reactions in order to build a comprehensive astrophysically relevant solid-state reactions network.

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