

## ION-MOLECULE REACTION STUDIES BELOW 80 K BY THE CRESU TECHNIQUE

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The basic principles of the CRESU technique (Cinétique de Réactions en Ecoulement Supersonique Uniforme) are presented. This technique allows ion-molecule reaction rate coefficients under true thermal conditions at interstellar temperatures. Various behaviors of both third-body association and binary reactions with temperature have been observed, including ion-polar molecule reactions whose rate coefficients sharply increase at very low temperatures.

### 1. INTRODUCTION

Since the pioneering flowing afterglow studies by Ferguson and co-workers (Albritton 1978), the development of the SIFT apparatus by Smith and Adams has been an important step in the knowledge of interstellar chemistry, giving numerous results at temperatures as low as 80 K on processes including isotope exchange and third-body association reactions (Adams and Smith 1984). More recently, lower temperatures have been attained in both ion trap (10 K) at JILA and helium-cooled flow drift tube (45 K) at Heidelberg. These techniques have given the first results at low temperatures on radiative association reactions for the former (Barlow, Dunn and Schauer 1984), and on third-body association reactions for the latter (Böhlinger and Arnold 1982). However, their use is limited by a condensation problem for most of neutrals. Another step is now achieved with the CRESU technique developed at Meudon, that is, the ability to measure rate constants with condensable neutrals under true thermal conditions in the range 8-70 K in helium buffer and 20-160 K in diatomic buffer (nitrogen or oxygen). Detailed descriptions of the technique being published elsewhere (Rowe et al. 1984a, b; Dupeyrat et al. 1985), only the basic features will be summarized here.

The low temperature is obtained by the isentropic expansion of a buffer gas, containing both ion parent and neutral reactant gases, through a suitably contoured Laval nozzle. Ions are created close downstream from the nozzle exit by an electron beam. Primary and product ions are monitored by means of a moveable quadrupole mass spectrometer

associated with a particle counting system. If the flow conditions are uniform (this is in fact the essential requirement of the technique) the rate constant is simply deduced from the exponential law governing the primary ion density versus the neutral reactant flow rate or the distance from the e-beam.

## 2. RESULTS

### 2.1. Association Reactions

The laboratory study of termolecular association reaction rates is of interest since the rates of the corresponding radiative processes can be inferred from them (see the theoretical works of Bates and Herbst). A good agreement between experimental data and calculations has been found down to 20 K for the reaction  $N_2^+ + 2 N_2 \rightarrow N_4^+ + N_2$  (1) whose rate coefficient obeys the relationship  $k(1) = 6.5 \times 10^{-29} (300/T)^{1.77} \text{ cm}^6 \cdot \text{s}^{-1}$ . The reaction  $O_2^+ + 2 O_2 \rightarrow O_4^+ + O_2$  (2) has also been examined but only lower limits have been reported at the lowest temperatures, i.e.  $k(2) \geq 1.0 \times 10^{-27} \text{ cm}^6 \cdot \text{s}^{-1}$  at 20 K (Rowe et al. 1984b).

### 2.2. Binary Reactions

Generally speaking all the studied reactions which are rapid at room temperature remain rapid in the range 10–100 K. It is in fact important to check the efficiency of reactions such as  $He^+ + N_2$  (3) and  $He^+ + CO$  (4) at interstellar temperatures. This has been done for reactions (3) and (4) and for  $He^+ + O_2$  (5),  $N^+ + CH_4$  (6) and  $N^+ + CO$  (7) down to 8 K. All these reactions do not show any significant departure of their rate coefficient from the Langevin value (Rowe et al. 1985) so that the simple induced-dipole model seems to work well for non or slightly polar neutrals.

However, the reaction  $N^+ + H_2$  (8) is a striking exception since its rate coefficient is represented by  $k(8) = 5.1 \times 10^{-10} \exp(-215/T(K)) \text{ cm}^3 \cdot \text{s}^{-1}$  for parahydrogen below 300 K (Marquette et al. 1985a), the 215 K value being interpreted as an endothermicity. This result is in agreement with those obtained by Adams and Smith (1985) and by Luine and Dunn (1985). Thus, this reaction is completely inefficient as starting process of  $NH_3$  synthesis in dense clouds although Adams et al. (1984) point out the fact that the  $N^+$  ions released from reaction (3) have 0.28 eV of kinetic energy, which is enough to overcome the endothermicity of reaction (5). They recommend a value of  $4.8 \times 10^{-10} \text{ cm}^3 \cdot \text{s}^{-1}$  for  $k(8)$ . In a recent paper, Viala (1985) used this value in a steady state model of dense clouds and noticed that the contribution of reaction (8) to the synthesis of nitrogen hydrides is negligible at all optical depths because of the low abundance of  $N^+$  ions.

On the other hand, reactions occurring slowly at room temperature exhibits an increase of the rate coefficient with decreasing temperature. A typical example is the reaction  $O_2^+ + CH_4 \rightarrow H_2COH^+ + H$  (9) with  $k(9) = 1.1 \times 10^{-7} T^{-1.8} \text{ cm}^3 \cdot \text{s}^{-1}$  below 200 K (Rowe et al. 1984a). Furthermore,  $k(9)$  reaches the Langevin limit when  $T \rightarrow 0$ . It was

thought that the product ion was protonated formic acid but more recent measurements of both reactivity of this product ion (Van Doren et al. 1985) and methane isotope effects (Barlow et al. 1985) indicate that it is rather methylene hyperoxy cation. All these results makes the mechanism of reaction (9) one of the actually better known.

Charge exchange reactions which are slow at room temperature can be another kind of process with a temperature dependent rate coefficient as shown by the bimolecular reaction  $N_2^+ + O_2$  (10):  $k(10) = 3.9 \times 10^{-10} \exp(-T(K)/147) \text{ cm}^3 \cdot \text{s}^{-1}$  below 360 K (Gaucherel et al. 1985). This result confirms and extends to extremely low temperatures a previous observed behavior of reactions of atmospheric interest (Lindinger et al. 1974), including reactions of  $O^+$  ions with nitrogen and oxygen (still not studied by the CRESU technique because of the influence of Penning and/or association reactions, see next section).

Particularly important reactions for interstellar chemistry are those involving permanent polar molecules. The following processes have been studied at 27 and 68 K (and 163 K for  $N^+$  reactions):  $He^+ + NH_3$  (11),  $H_2O$  (12);  $C^+ + NH_3$  (13),  $H_2O$  (14);  $N^+ + NH_3$  (15),  $H_2O$  (16). They all exhibit a marked temperature dependence as listed in the table which gives the power laws deduced from these measurements (Marquette et al. 1985b) and from previous works at 300 K (Albritton 1978). The column at the right is the ratio of rate coefficients at 10 K deduced from these laws on the values used by Prasad and Huntress (1980). The most outstanding features are: i) reaction (12) is considerably underestimated; ii) values greater than  $10^{-8} \text{ cm}^3 \cdot \text{s}^{-1}$  are attained, in particular for reaction (14) which is important for the coupling of O-H and C-O chemistries; iii) reaction (13) is still more efficient than expected, making the problem of  $NH_3$  synthesis more questionable; iv) reaction (15) should be included in models as ammonia destruction process. Item ii) is certainly the most remarkable whereas recent SIFT experimental confirm ACCSA theoretical works on HCN and HCl reactions. Ion-polar molecule reaction rate coefficients can even reach values as high as  $10^{-7} \text{ cm}^3 \cdot \text{s}^{-1}$  at interstellar temperatures because they are j-dependent and in some cases larger at 10 K than the extrapolation of experimental power laws (Clary et al. 1985; Adams et al. 1985).

### 3. CONCLUSION AND PERSPECTIVES

The CRESU apparatus provides actually data on reactions of astrophysical interest. However, the versatility of the technique is restricted by the influence of metastable helium atoms inducing Penning reactions yielding, for example,  $O^+$  ions. Furthermore, the presence of the ion parent gas in the flow yields secondary processes (in particular, association reactions). The next improvement of the apparatus would be a selective injection of ions, giving the ability to measure branching ratios and to particularly study ion-dipole reactions and other processes such as isotope exchanges.

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Table 1. Units are  $\text{cm}^3 \cdot \text{s}^{-1}$ , parentheses are powers of ten.

React. No	power law	k/k <sub>PH</sub>
(11)	1.76(-8)T <sup>-0.42</sup>	3.3
(12)	9.41(-8)T <sup>-0.94</sup>	24.7
(13)	1.14(-8)T <sup>-0.29</sup>	2.5
(14)	8.84(-8)T <sup>-0.63</sup>	7.7
(15)	7.05(-8)T <sup>-0.77</sup>	-
(16)	5.55(-8)T <sup>-0.52</sup>	6.4

## DISCUSSION

HERBST: Are you planning to study reactions involving very polar neutrals such as HCN?

MARQUETTE: It is effectively planned to study reactions down to 27K with HCN and also HCL and other polar molecules such as methanol and acetonitrile. In fact, the problem is the production of ions such as  $H_3^+$  or  $O_2^+$  in the buffer. Actually, the easiest to produce are  $He^+$  (evidently) and  $N^+$  and  $C^+$  from  $He^+ + N_2$  and  $He^+ + CO$ , respectively. The injection of mass selected ions is expected to solve this problem.

JACKSON: How do you separate reactions due to knock on collisions versus the true thermal reactions?

MARQUETTE: Your question refers to molecular beams for which this problem is important. In the present case the jets that we use are stationary uniform supersonic flows and very different from molecular beams. They are continuous, with L. T. E. for translation-rotation, superposed on the mean flow velocity. The particles have an isotropic thermal motion, ensuring the reactants to be thermalised in a few microseconds while the time available for the reaction lies in the range  $10^{-4} - 10^{-3}$  s.

MITRA: How do you measure the temperature in your reaction?

MARQUETTE: It is determined in two ways. The first is based on the assumption that the flow is isentropic and thus the stagnation temperature in the nozzle reservoir,  $T_0$ , and the flow temperature,  $T$ , are related by the equation

$$\frac{T_0}{T} = s + \frac{\gamma-1}{2} M^2$$

where  $\gamma$  is the ratio of specific heats of the buffer gas and  $M$  the Mach number. It is possible to know  $M$  by an impact pressure probe along the axis of the isentropic core. Thus  $T$  is known by measuring  $T_0$  with a thermocouple. The second method is based on the fact that uniform supersonic flows have streamlines parallel to their axis. The Navier-Stokes equation immediately yields a zero radial pressure gradient and, hence, the flow pressure and the test chamber pressure are equal. We are able to determine the radial density profile of the flow by an electron beam - induced fluorescence technique. Simply applying the perfect gas law, we deduce the flow temperature from the measurement of the test chamber temperature, i.e., the room temperature (for details, see Dupeyrat et al. 1985). The agreement between the two methods is very good. In addition, some reactions act as thermometer like  $N^+ + H_2$  at 20 K; it is possible to measure its rate coefficient in both He and  $N_2$  buffers, with different physical conditions (pressure, primary ion production mechanism). The good agreement between the two results assesses the internal consistency of the temperature determinations.