

CHEMICAL REACTIONS IN ASTROCHEMISTRY

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ABSTRACT. This paper is devoted to chemistry in the gas phase dealing firstly with ion-molecule reactions at extremely low temperature. The experimental techniques that have been used in this field are shortly presented and the reactions that have been studied using the CRESU(S) method reviewed. In the second part, the most recent measurements concerning dissociative recombination are discussed, including studies of branching ratio and new determination of the rate coefficient for H_3^+ ions.

1. Introduction

As shown throughout these proceedings, it is now apparent that the physics and chemistry of interstellar clouds is far more complicated than the simple picture described by the first gas phase models of a quiescent, stationary cloud. Chemistry on grain surfaces and in shocked regions cannot be neglected in the processes that lead to molecule formation and the evolution of the cloud itself has to be considered. However gas phase chemistry is certainly involved in the formation of a major part of the molecules observed in interstellar space. In the thousands of chemical and physical processes that have been considered in various models there is always a lack of experimental data, leading to major uncertainties concerning the predicted abundances of various species. The last three years have brought remarkable breakthroughs in two fields : ion-molecule reaction rate coefficients have been measured down to extremely low temperatures and, in a few cases, the product channels and branching ratio in the dissociative recombination (hereafter DR) of polyatomic ions have been determined. On an other hand a large controversy broke out concerning the value of the DR rate coefficient of H_3^+ , which plays a key role in cloud chemistry. The most recent measurements yield a large coefficient in contradiction with the extremely small value reported by Adams and Smith [1].

2. Ion-molecule reactions at extremely low temperature

2.1. EXPERIMENTAL TECHNIQUES

The study of rate coefficients at extremely low temperature is very challenging from an experimental point of view and only four research groups have succeeded in such measurements. Cryogenic cooling has a great limitation since neutral reactants other than helium and hydrogen condense on the walls of the reaction cells. However, it has been used in the static drift tube of H. Böhringer et al [2] and in the ion trap of G. Dunn and co-workers [3]. These experiments were difficult to operate and are no longer used. Another cooling strategy is to generate the very low temperature with a supersonic expansion. Then it is possible to use neutral reactants in supersaturation conditions. The CRESU (and CRESUS which allows mass selection of the ions) apparatus has been described in detail elsewhere [4], [5], [6]. The most important feature of this experiment is that true thermal conditions exist locally (excepted for H_2 and D_2 rotational levels). The rotational levels are in thermal equilibrium with a kinetic temperature which corresponds to a local Maxwell-Boltzmann distribution of velocity. This is not the case in the free jet experiment recently developed in Tucson (USA) by M. Smith et al [7]. In this last case, the jet is obtained by expansion of premixed gases through a small orifice and there are strong density gradients in the flow. Consequently there is not a real local thermodynamical equilibrium in this experiment and the mean effective estimated rotational "temperature" is often far greater than the effective kinetic "temperature".

2.2. MAINS RESULTS CONCERNING ION MOLECULE REACTIONS

The rate coefficient of many ion-molecule reactions can be calculated as a capture rate coefficient, i.e. using only the long range part of the potential energy surface on which the reaction takes place.

For molecules having no permanent dipole moments, the ion-induced dipole potential leads to the Langevin formula which predicts a rate coefficient independent of temperature. For polar molecules the calculation of the capture rate coefficient is far more complicated and can be performed using various methods which have been reviewed elsewhere [8]. Table 1 summarizes the CRESU results obtained for reactions between ions and polar molecules and shows that a strong increase of the rate coefficient is obtained at low temperature, which is well reproduced by theoretical calculations. An interesting feature pointed out by theory is the strong influence of rotational state on the reactivity. This effect can be highlighted when considering the measurements of the rate coefficient of $NH_4^+ + NH_3$ at 2.5 K by Hawley et al. [7] using the Tucson apparatus, yielding a much lower value than expected on theoretical basis. This can be explained if one considers that rotation in this experiment is not fully relaxed, and corresponds to a temperature that could be ten times larger than the kinetic one.

CRESU(S) measurements have shown that, when the rate coefficient of an ion-molecule reaction is much smaller than the capture rate it often increases at lower temperatures, sometimes approaching k_c at temperatures close to 0 K [9], [10], [11]. However this is not a general rule as shown by the fact that the $He^+ + H_2$ reaction remains extremely slow at low temperature [12].

A very interesting reaction from an astrochemical point of view is the reaction of N^+ with H_2 . It has been studied down to 8 K using normal and para hydrogen as well as HD and D_2 and exhibits a strong decrease of the rate coefficient with temperature. Analysis of the results shows that the endothermicity of the reaction $\text{N}^+ + \text{H}_2 \longrightarrow \text{NH}^+ + \text{H}$ for ground state reactants and products is 18 ± 2 meV [13]. Implication of this finding for interstellar ammonia formation has been discussed by Herbst et al. [14].

An important class of ion-molecule reaction is radiative association. Unfortunately the few results available to date are often contradictory as in the case of $\text{CH}_3^+ + \text{H}_2$. The results obtained by Barlow et al. [15] and Gerlich and Kaefer [16] at respectively 13 and 80 K would imply a strong temperature dependence which is extremely unlikely on the basis of theoretical considerations [17] and of the CRESUS study of the analogous ternary association between 20 and 80 K [18].

3. Dissociative recombination of molecular ions

3.1. BRANCHING RATIOS IN DISSOCIATIVE RECOMBINATION

A good knowledge of the branching ratios in dissociative recombination is extremely important for interstellar chemistry. Only recently a few measurements have been performed concerning the yield of OH radicals or H atoms in DR reactions ([19], [20], [21]) using either laser induced fluorescence or VUV resonance absorption techniques. One of the major findings of these studies was that the channel leading to H_2O in H_3O^+ DR has a branching ratio lower than 0.34. Also they showed that H_3O^+ and OCSH^+ cannot be an important source of H_2S and OCS respectively in interstellar clouds, since H atoms production is small in recombination of these ions.

3.2. RATE COEFFICIENTS IN DISSOCIATIVE RECOMBINATION

Although a wide variety of reliable techniques now allows α values to be determined, some important contradictions remain as in the various studies concerning the DR rate coefficient of H_3^+ (see table 2).

A new Flowing Afterglow apparatus has been used by the author and his coworkers to study the DR of several ions including H_3^+ . The new feature of this apparatus is that a movable mass spectrometer allows the ion densities to be measured in the recombination zone. These measurements confirmed Amano's results, i.e. that dissociative recombination of H_3^+ ions with low vibrational levels (including $v=0$) is in the range $1.1 - 1.5 \cdot 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ ([22], [23]). Other ions studied with this apparatus include HCO^+ and HCS^+ [24], [25] with $\alpha = 2.4 \cdot 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ and $7 \cdot 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ respectively.

A detailed discussion of the problems associated with the vibrational states of the ions is given in the references above.

Table1: reaction rates for ion-polar molecules ($10^{-9}\text{cm}^3\text{ s}^{-1}$), uncertainty is $\pm 30\%$

reactants	T=27K	T=30K	T=68K	T=300K
He ⁺ + HCl	11.0		4.6	3.3
He ⁺ + SO ₂	8.2		6.5	4.3
He ⁺ + H ₂ S	5.5		4.6	2.8
He ⁺ + NH ₃	4.5		3.0	1.65
He ⁺ + H ₂ O	4.3		1.8	0.48
C ⁺ + HCl	3.8		1.9	1.0
C ⁺ + SO ₂	5.7		4.1	2.3
C ⁺ + H ₂ S	4.8		3.1	1.7
C ⁺ + NH ₃	4.6		3.2	2.3
C ⁺ + H ₂ O	12.0		5.2	2.5
H ₃ ⁺ + SO ₂		11.0		
H ₃ ⁺ + H ₂ S		6.5		3.4
H ₃ ⁺ + NH ₃		9.1		4.2
N ⁺ + NH ₃	5.2		3.2	2.4
N ⁺ + H ₂ O	9.9		6.0	2.8

Table2: Summary of the main results for $\alpha(\text{H}_3^+)$ at 300K

$\alpha(\text{H}_3^+)$ ($\text{cm}^3\text{ s}^{-1}$)	method	reference
$2.3 \cdot 10^{-7}$	$\mu\text{wa-ms}^{\text{a}}$	[26]
$2.5 \cdot 10^{-7}$	inclined beam	[27]
$\approx 2.1 \cdot 10^{-7}$	merged beam	[28]
$1.5 \cdot 10^{-7}$	ion trap	[29]
$2.1 \cdot 10^{-7}$	merged beam	[30]
$\leq 2 \cdot 10^{-8}$	FALP	[31]
$1.5 \cdot 10^{-7}$	$\mu\text{wa-ms}^{\text{a}}$	[32]
$\leq 10^{-11}$	FALP	[1]
$\approx 2 \cdot 10^{-8}$	merged beam	[33]
$1.8 \cdot 10^{-7}$	I.R. spectroscopy	[34]
$1.5 \cdot 10^{-7}$	FALP	[23]

^a: $\mu\text{wa-ms}$ = microwave afterglow mass spectrometer

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QUESTIONS AND ANSWERS

D.A.Williams: How many H-atoms per reaction arise from CH_5^+ recombination?

B.Rowe: This is one of the cases where all the measurements have a very good internal consistency (between Rennes and Birmingham experiments and with various precursor ions). The yield of H atoms is close to 1.2.

A.Dalgarno: Will measurements be possible of reactions of ions like He^+ with reactive species such as atomic oxygen and atomic nitrogen?

B.Rowe: There is in principle no difficulties in doing reactions with oxygen and nitrogen atoms (carbon is much more difficult). However, if the reaction of the ion with the corresponding diatomic molecules is fast and the reaction with the atom slow, the measurement could be extremely difficult.

M.Guelin: The new recombination rate value you derive for H_3^+ restores the very low limits as the electron density derived in the dark cloud cores from DCO^+ and $H^{13}CO^+$ observations (e.g. Guelin et al. 1982, *Astron.Astrophys.* 107,107). These limits ($10^{-9} < x_e < few \times 10^{-7}$) have important implications as metal depletion, ambipolar diffusion time scales, cosmic ray ionization rate, etc.

B.Rowe: I thank you for this comment and I am glad to see that laboratory works are really useful in astrochemistry.