

Gas-Phase Reactions at Low Temperatures: Towards Absolute Zero**

Ian W. M. Smith,* Ian R. Sims and Bertrand R. Rowe

Abstract: Very recently, methods have been developed for studying the rates of chemical reactions between electrically neutral species in the gas phase at temperatures as low as 13 K. Here we review this exciting development in gas-phase chemical kinetics. Emphasis is placed on the importance of the information which the experiments have provided, both from the viewpoint of posing new questions about the factors which control chemical reactivity and because of their relevance to the modelling of molecular synthesis in interstellar clouds.

Keywords: gas-phase chemistry · interstellar chemistry · kinetics · low-temperature chemistry · radicals

Introduction

At the molecular level, as the temperature of a gas is lowered, its average energy content falls. Because the internal motions, vibrations and rotations are quantised, the distributions over these quantum states change according to the Boltzmann laws. If these distributions can be measured spectroscopically, the temperature can be inferred—we have a “molecular thermometer”. In addition, the distribution of speeds in a gas changes: the average speed and the spread of speeds become less as the temperature falls, whilst the actual values depend on the mass of the molecules as well as the temperature. Gases eventually condense when the relative motion of their molecules becomes insufficient to overcome the attractive forces between them. Consequently boiling points depend on both relative molecular mass and on the strength of the intermolecular interactions: water and

ethanol have unusually high boiling points for their molecular masses because of their unusually strong intermolecular attractions.

A century ago, one of the major aims of physical chemists was to liquefy the “permanent gases”, and to understand the processes by which this was achieved. An important milestone was the liquefaction of air independently by Hampson and Linde in 1895, and this work reached its zenith—and was complete—when Kammerlingh Onnes succeeded in liquefying helium in 1905. The low temperatures required were reached by expansion along with cooling by gas that had previously undergone expansion. In view of what follows, it is worth emphasising that the crucial process for the achievement of low temperatures was *expansion*. Gases were made to do work against either an external medium or against their own intermolecular forces, or both.

In recent years, physical chemists have developed techniques based on gaseous expansions to study gas-phase species, isolated molecules, and small clusters at extremely low temperatures *before* they condense. Nearly all of these experiments have made use of extreme expansions from a high-pressure reservoir through a small orifice into a high vacuum. The frequency of collisions during the expansion is sufficient to reduce the translation–rotational temperature, in some cases to below 1 K, and to form small “fragile” clusters, held together by weak van der Waals forces,^[1] but is insufficient to cause real condensation. The medium produced in these free jet expansions is not promising for kinetic studies, since downstream of the nozzle the gas density is very low and continually changing. It was B. R. Rowe who realised that the dense uniform supersonic flow created downstream from a Laval nozzle was a much more promising medium for investigating gas-phase reactions, and his group applied it to the study of ion–molecule reactions at temperatures down to 8 K.^[2] In collaboration with Rowe’s group, we have developed a CRESU apparatus (Cinétique de Réaction en Ecoulement Supersonique Uniforme) for studying reactions between electrically neutral species^[3, 4] and it is these experiments, their results and their importance which are briefly reviewed here.

Discussion

Gas Reactions at Low Temperatures—The Reasons Why! Our aim has been to measure the rates of chemical reactions in the gas phase at temperatures far below those at which the reactants

[*] Prof. I. W. M. Smith, Dr. I. R. Sims
School of Chemistry, The University of Birmingham
Edgbaston, Birmingham B15 2TT (UK)
Fax: Int. code +(121)414-4426
e-mail: smithiwm@birmingham.ac.uk

Dr. B. R. Rowe
DPAM, URA 1203, CNRS
Université de Rennes
Campus de Beaulieu
F-35042 Rennes Cedex (France)

[**] From a lecture delivered by I. W. M. S. at the meeting of the British Association for the Advancement of Science at the University of Birmingham, September 9–13, 1996.

involved have an appreciable vapour pressure. In other words, experiments must be performed under supersaturated conditions. It is worth remembering that, broadly speaking, as molecules get larger their chemistry gets richer but their boiling points also rise. Before seeing how the experiments are performed, it may be worthwhile to examine the motives for this work.

First, there is the excitement of facing and overcoming a new experimental challenge; of doing experiments under quite new physical conditions. This motive is coupled with the belief, not unusual amongst scientists, that such an exploration will uncover fresh and unexpected phenomena and thereby our knowledge and understanding of the processes under investigation will be improved. The temperature dependence of rate constants, $k(T)$, for chemical reactions is often discussed in terms of the celebrated Arrhenius equation: $k(T) = A \exp(-E_a/RT)$, where E_a is the activation energy and is associated with the energy required to reorganise the chemical bonds as reagents are transformed into products. Clearly, in any reaction for which this equation holds and the value of E_a is significant, the rate constant must become vanishingly small as the temperature is reduced towards absolute zero. Such a situation is illustrated in Figure 1 for the reaction between CN radicals and H_2 , where the activation energy,

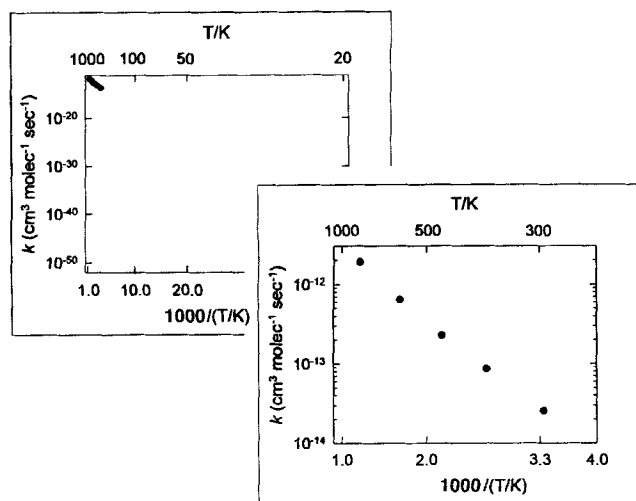


Figure 1. Arrhenius plots of $\ln(k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ versus $1000/(T/K)$ for the reaction between CN radicals and H_2 . The existence of a significant activation energy causes the rate constant to become vanishingly small at low temperatures.

derived from experiments at room temperature and above, is 17.2 kJ mol^{-1} . Therefore the kinetics of any reaction which is to be fast at ultra-low temperatures must be “non-Arrhenius”. Candidates include: a) ion–molecule reactions; b) reactions between free radicals; and c) some reactions of radicals with unsaturated species.

A second major reason for interest in the kinetics of gas-phase reactions at ultra-low temperatures is their relevance in planetary and interstellar environments. The lowest temperature found in the Earth’s atmosphere is $\approx 180 \text{ K}$, far above the temperatures which are reached in our experiments. Nevertheless, for many atmospherically important reactions, conven-

tional techniques for studying their kinetics fail at temperatures well above 180 K and measurements at lower temperatures are valuable. In addition, the temperatures in the atmospheres of other planets, or more particularly their moons such as Titan and Triton, are much lower. In all cases, a knowledge of chemical reaction rates is required to understand the rich chemistry and photochemistry which leads to the observed molecular abundances.^[6]

Perhaps the most spectacular requirement for kinetic information at ultra-low temperatures is in connection with the chemistry in interstellar clouds.^[5] Approximately 100 types of molecules have now been identified in these vast objects by radioastronomical techniques and it is generally agreed that these species are synthesised *in situ*; they are not generated in hotter denser regions and transported to the clouds. The temperatures in dark interstellar clouds, where most molecules are found, lie in the range $10\text{--}50 \text{ K}$. Until the impact of the work which is described here, it was generally believed that the chemistry was driven almost entirely by processes involving electrically charged species: ionisation by cosmic rays, ion–molecule reactions, dissociative recombinations, etc. The inclusion in chemical models of extensive neutral–neutral chemistry has had a profound impact on predicted molecular abundances.^[6]

Gas Reactions at Low Temperatures—How They Are Studied:

How They Are Studied: In a CRESU apparatus (Figure 2), samples of gas are prepared by expansion through a convergent–divergent Laval nozzle. Each nozzle is constructed, for a particular “carrier gas”, to create a preselected combination of density and temperature in the supersonic flow of gas downstream from the nozzle exit. The use of several nozzles, each of which can be mounted on the gas reservoir, enables a range of conditions to be created. The gas mixture prepared in the reservoir contains three constituents—a very small concentration of the photochemical precursor for a free-radical reagent (e.g., NCNO for CN radicals), a larger, but still small, concentration of the coreagent, and the carrier gas (He, Ar or N_2), which is present in great excess.

Within the cooled gas sample, we implement the well-established pulsed laser photolysis (PLP)–laser-induced fluorescence (LIF) technique for studying the rates of radical reactions. One

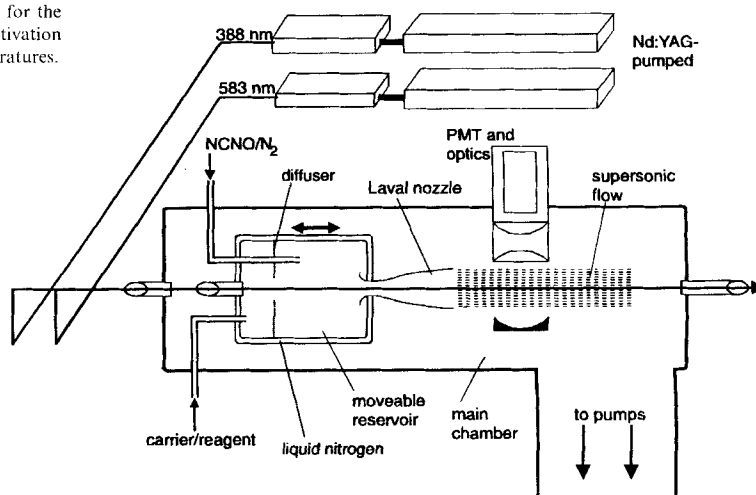


Figure 2. Schematic diagram of the CRESU apparatus used in the study of neutral–neutral reactions at the University of Rennes.

pulsed laser, fired first, photolyses a fraction of the precursor (for example, NCNO for CN radicals). The frequency of a second pulsed (dye) laser is tuned to an absorption in the electronic spectrum of the free radical, causing it to fluoresce. The intensity of the LIF signal is proportional to the concentration of the radical, so by varying the time delay between the first laser pulse and the second, one can observe how the radical's concentration varies as it is removed by reaction with the coreagent. Experiments at different concentrations of the coreagent enable the rate constant for the reaction to be determined.

Gas Reactions at Low Temperatures—Results: The unique CRESU apparatus at the University of Rennes has now provided rate constants for upwards of twenty elementary chemical reactions between neutral species. Table 1 identifies these reactions and lists the lowest temperatures for which rate constants have been determined.

Table 1. The minimum temperatures for which rate constants have been measured for reactions of CN, OH and CH radicals and for the removal of vibrationally excited CH ($v = 1$).

	CN	OH	CH	CH ($v = 1$)
CH ₄	–	178	23	–
C ₂ H ₆	25	138	23	–
NH ₃	25	–	23	–
H ₂	–	–	–	23
D ₂	–	–	13	23
HBr	–	23	–	–
N ₂	–	–	–	23
CO	25	80	–	23
C ₂ H ₂	25	–	23	–
C ₂ H ₄	–	–	23	–
butenes	–	23	23	–
O ₂	13	–	13	–
NO	99	23	13	–

For all these reactions, the general trend is for the rate constants to increase as the temperature is lowered—exactly contrary to what the Arrhenius equation would lead one to anticipate—and the rate constants at the lowest temperatures are close to the values which one would expect on the basis of simple collision theory. (In assessing this statement, the reader should be aware that our method can only measure rate constants for fast reactions!) There is no space here to do all these results justice, so we have chosen just three examples, for which results are shown in Figure 3.

The reaction between CN and O₂ was the first neutral–neutral reaction to be studied in a CRESU apparatus.^[31] Its rate has now been determined in direct experiments spanning the temperature range 13–3800 K! Between 750 K and 23 K the rate constant fits the form $k(T) = k(298 \text{ K})(298/T)^n$, with $n = -0.6$. Doubtless, and not surprisingly, it proceeds by the initial and transitory addition of CN to O₂ (both reagents are free radicals, in that they possess unpaired electrons) followed by the breakdown of the NCOO complex to NCO + O (although NO + CO may be minor products).

The kinetic behaviour of the reaction between CN and C₂H₂ is similar to that of several reactions of unsaturated molecules with radicals.^[7–9] When the long-range, electrostatic, forces are

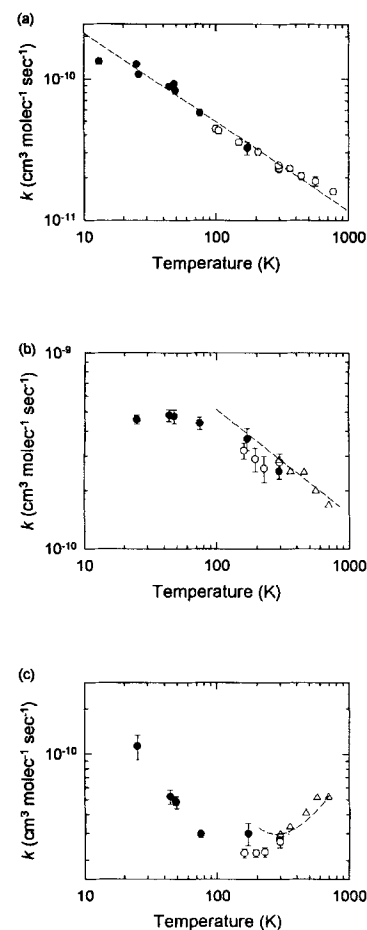
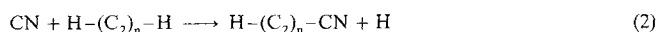
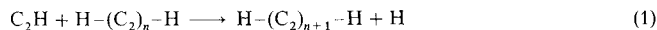


Figure 3. Variation of the rate constants with temperature for three reactions of different types: a) between two radicals, CN + O₂; b) between a radical and an unsaturated molecule, CN + C₂H₂; c) between a radical and a saturated molecule, CN + C₂H₆.

especially large, it appears that the rate constants reach a limiting value and indeed they may even decrease as the temperature is lowered further. It seems that the rate of reaction is being controlled entirely by the rate at which the two reagents are “captured” and brought into intimate contact by the long-range attractive potential between them, behaviour which seems to be common in reactions which occur at or near the collision rate at low temperatures. However, in other cases, such as the CN + O₂ reaction, it is not just the limiting long-range potential which is important; the transition-state region moves to smaller inter-reagent separations, where chemical forces of attraction are beginning to act.

The reaction between CN and C₂H₂ is one of replacement, the products being HC₂CN + H. Cyanopolynes are among the largest and most interesting species which have been found in the ultra-cold environment of interstellar clouds. Our results, along with a simple chemical argument and indirect evidence, suggest that they may be synthesised in sequences of reactions involving CN and the isoelectronic radical C₂H. Although the rate constants for reactions between C₂H and acetylene and polyynes have not been determined at ultra-low temperatures, they are known to be rapid down to 170 K, and analogy with the reactions of CN suggests that they will remain rapid at still lower temperatures. If this is so, then reactions such as those in

Equations (1) and (2) could be responsible for the synthesis of the cyanopolyynes observed in interstellar clouds.



The third example, chosen to illustrate the diversity of behaviour found in our experiments, is the reaction between CN radicals and C_2H_6 [Eq. (3)]. As it is an exothermic H-atom



abstraction reaction, one could be forgiven for expecting that its rate constant would vary with temperature according to the simple or modified Arrhenius equation. In practice, as the results in Figure 3c show, the rate constants show a complex dependence on temperature, increasing from a minimum value at ca. 200 K as the temperature is either raised or lowered.^[7] The rate constant at 25 K is higher than at any other temperature below 1000 K. This high value of the rate constant at such a low temperature shows clearly that there cannot be any maximum along the path of minimum energy leading from reactants to products. The variation of $k(T)$ with temperature must reflect subtle changes in the nature and location of the transition-state bottleneck as the energy and angular momentum in the colliding systems change. Alternatively, one could say that the reaction rate is controlled by entropic factors whose variation determines how the rate constant changes with temperature.

Summary and Prognosis

The implementation of the PLP-LIF technique in the super-cold environment provided in a CRESU apparatus by controlled expansion through a Laval nozzle has enabled us to

measure the rates of elementary gas-phase reactions at temperatures far lower than have previously been accessed. The results obtained have aroused considerable interest from two groups of "beneficiaries": theoretical chemists interested in the factors which control chemical reactivity, and astrophysical chemists who attempt to reproduce the species abundances in interstellar clouds through the use of chemical models.

The unique apparatus that was constructed in Rennes, and which has been used in all the experiments which are referred to in this short review, now has a British cousin in the University of Birmingham. The versatility of the CRESU technique has been further demonstrated by very recent measurements a) in Birmingham, on state-to-state energy transfer in NO-He collisions down to 7 K,^[10] and b) in Rennes, on the first reactions of metal (Al) atoms.^[11] Many exciting problems remain to be solved!

Received: April 8, 1997 [C 663]

-
- [1] *Faraday Discuss. Chem. Soc.* **1994**, *97*, *Structure and Dynamics of Van der Waals Complexes*.
- [2] B. R. Rowe in *Rate Coefficients in Astrochemistry* (Eds.: T. J. Millar, D. A. Williams), Kluwer, Dordrecht, **1988**, p. 135.
- [3] I. R. Sims, J.-L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, P. Bocherel, B. R. Rowe, I. W. M. Smith, *J. Chem. Phys.* **1994**, *100*, 4229.
- [4] I. R. Sims, I. W. M. Smith, *Ann. Rev. Phys. Chem.* **1995**, *46*, 109.
- [5] a) E. Herbst, *Ann. Rev. Phys. Chem.* **1995**, *46*, 27; b) D. A. Williams, *Chem. Eur. J.* **1997**, *3*, 1929.
- [6] E. Herbst, H.-H. Lee, D. A. Howe, T. J. Millar, *Mon. Not. R. Astron. Soc.* **1994**, *268*, 335.
- [7] I. R. Sims, J.-L. Queffelec, A. Defrance, D. Travers, B. R. Rowe, L. Herbert, J. Karthaus, I. W. M. Smith, *Chem. Phys. Lett.* **1993**, *211*, 461.
- [8] I. R. Sims, P. Bocherel, A. Defrance, D. Travers, B. R. Rowe, I. W. M. Smith, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 1473.
- [9] A. Canosa, I. R. Sims, D. Travers, I. W. M. Smith, B. R. Rowe, *Astron. Astrophys.* **1997**, *323*, 644.
- [10] P. James, I. R. Sims, I. W. M. Smith, *Chem. Phys. Lett.* **1997**, *272*, 412.
- [11] A. Canosa, S. LePicard, B. R. Rowe, personal communication.