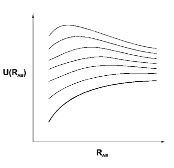
The Liversidge Lecture 2001–02. Chemistry amongst the stars: reaction kinetics at a new frontier



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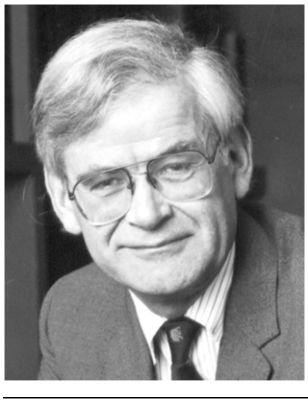
Received 2nd January 2002
First published as an Advance Article on the web 5th April 2002

Over the past decade, experiments in the Universities of Rennes and Birmingham have provided rate constants for over 40 reactions of molecular and atomic radicals with neutral molecules at temperatures down to 13 K using the CRESU (*cinétique de réaction en écoulement supersonique uniforme*) technique. The demonstration that reactions between electrically neutral species can be extremely rapid at these very low temperatures has excited interest both from theoreticians and from those seeking to understand the chemistry that gives rise to the 120 or so molecules that have been identified as being present in dense interstellar clouds. This laboratory work, and its astrochemical and theoretical contexts, are reviewed here. In addition, I deal briefly with the present limitations of the experiments and how they might be overcome in future work.

1 Introduction

The principal aim in this article is to provide a personal review of experiments that have, over the past decade, enabled the rates of elementary gas-phase reactions to be measured down to what were previously unattainably low temperatures—this is the 'new frontier' of my title. These measurements have generated considerable theoretical interest—how can reactions be so fast at such low temperatures and what factors control their rates? In addition, they have demonstrated that reactions between electrically neutral species cannot be neglected when attempts are made to explain the presence of molecules in the extreme environments found in interstellar space. Before describing the experimental method that allows one to perform kinetic studies on chemical reactions at temperatures down to almost 10 K, and discussing some of the results that have been obtained in these measurements, I shall briefly describe the astrochemical context of these novel measurements. For further details about the observation and formation of interstellar molecules, the reader is referred to a recent *Chemical Society Review* by Herbst,[1] which carries the title '*The chemistry of interstellar space*'.

Ian Smith obtained his BA and PhD degrees from the University of Cambridge. After post-doctoral work with Professor John Polanyi, he returned to Cambridge where he was successively University Demonstrator and University Lecturer in the Department of Physical Chemistry. In 1985 he moved to the University of Birmingham as Professor of Physical Chemistry and he became Mason Professor in 1991. Ian Smith has wide-ranging interests in the fundamentals and applications of gas-phase processes. He has been awarded the Polanyi Medal of the RSC Gas Kinetics Group, the RSC Special Award in Reaction Kinetics, and a Tilden Medal and Lectureship. He was elected a Fellow of the Royal Society in 1995. With his collaborators, he was awarded one of the 1st Descartes Prizes (EU, Brussels). He is the Royal Society of Chemistry's Liversidge Lecturer for 2001–02 and is currently President of the Faraday Division of the Royal Society of Chemistry.



2 The astrochemical context

When one observes the night sky visually, or with conventional photographic plates, one obtains a selective view of our astronomical surroundings. Our eyes are only sensitive to a narrow part of the electromagnetic spectrum and we therefore observe stars, like our Sun, whose surface temperatures are in the range 1000–10000 K and therefore emit radiation which peaks in the visible part of the spectrum. In such environments, matter will generally be present as ionised atoms. Any molecules that might form are likely to be dissociated and the fragments ionised on astronomically short time-scales.

On this basis, it should come as no surprise that molecules are found in colder regions of space and that they are observed by the deployment of instruments that are sensitive to radiation of longer wavelengths than the visible. Most molecules in the interstellar medium have been identified through the use of what are conventionally referred to as 'radio-telescopes' operating at wavelengths around 1 mm, equivalent to frequencies of some tens of GHz. Fortunately, Earth's atmosphere is transparent to such radiation so the telescopes can be placed on the ground. Increasing use is now being made of spaced-based spectrometers, such as those on the infrared space observatory (ISO) that are sensitive in the infrared.[2] They can observe non-polar molecules and can probe rather warmer regions of space.

Mm-wave instruments can be employed in two astrochemically useful modes. In both, molecules are detected by observing the emission of radiation characteristic of the spacing between their rotational levels. First, the detector can be tuned to a frequency that corresponds to one in the rotational spectrum of a common molecule and the sky scanned to find those regions where this molecule is common. Fig. 1 shows the results of such a search using the $J = 1 \rightarrow J = 0$ transition in CO which is the second most abundant molecule in the interstellar medium (ISM), after H_2. What this diagram indicates is that molecules

DOI: 10.1039/b200017m

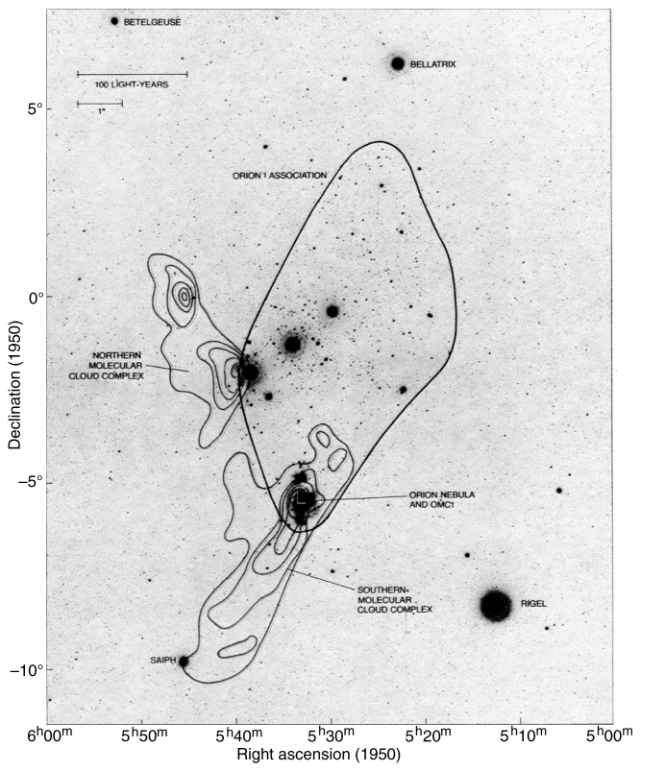


Fig. 1 'Radio map' of the two giant molecular clouds in the constellation of Orion (the three black images in line are the stars in Orion's belt). The contour lines show the intensity of emission in the $J = 1 \rightarrow J = 0$ rotational transition in carbon monoxide. The enormous size of these clouds can be gauged by the scale in the top left of the diagram. (Reproduced, with permission, from C. G. Wynn-Williams, *Sci. Am.*, 1981, **254**, 31, and by kind permission of the Harvard College Observatory.)

are found in the ISM principally in huge aggregates—molecular interstellar clouds (ISCs).

In their second operational mode, mm-wave telescopes perform spectroscopy. They are pointed in a promising direction, for example towards the two ISCs in the Orion constellation that are shown in Fig. 1, and signals are recorded as the frequency to which the detector is sensitive is scanned. Many molecular emission lines have been observed in this manner and, by comparison with laboratory spectra, these lines have been assigned to their molecular emitters. Principally in this way, over 120 molecules, which are shown in Table 1, have been identified in ISCs.[3] It should be stressed that Table 1 only lists those molecules for which the identification is based on high resolution spectroscopic measurements and for which the assignment is, therefore, reasonably secure. It does not, for example, include possible carriers of the diffuse interstellar bands.[4]

A number of features of the interstellar molecules listed in Table 1 are worthy of remark. The list is dominated by species containing carbon and most of the molecules are highly unsaturated, despite the overwhelming abundance of hydrogen in the environment. Some ions have been observed, though the majority of molecules are electrically neutral. Finally, it is worth pointing out that many of the species are free radicals; that is, they possess odd electrons and might be expected, at least under normal conditions, to show high reactivity.

Spectroscopic observations also provide information about the physical conditions in ISCs; for example, the relative intensities of different lines from the same molecule can be used to estimate the temperature in the source.[1] The greatest number and variety of molecules are found in *dense* ISCs, where the molecular density is typically 10^4 molecule cm^{-3} and the temperature is between 10 and 50 K. Within such clouds, which are the birthplace of new stars, hotter and denser regions are formed as gravity pulls the matter together creating higher densities and temperatures. The molecular concentration in these ISCs (much lower than the best 'ultra-high vacuum' that can be achieved in Earth-bound laboratories) is 'dense' in comparison with the average molecular density of *ca.* 1 molecule cm^{-3} throughout the ISM. Finally, it should be pointed out that, in these clouds, there is also a relatively high density (*ca.* 1 m^{-3}!) of particulate matter: *interstellar grains* or *dust*. This solid matter, which blocks out visible light making

Table 1 Molecules observed in interstellar and circumstellar environments (June 2001)[a]

N									
2	3	4	5	6	7	8	9	10	11
H_2	H_3^+	NH_3	CH_4	CH_3OH	CH_3NH_2	$HCOOCH_3$	$(CH_3)_2O$	$(CH_3)_2CO$	$\mathit{HC_8CN}$
$\mathbf{CH}$	$\mathbf{CH_2}$	H_3O^+	SiH_4	CH_3SH	$\mathit{CH_3CCH}$	$\mathit{CH_3C_2CN}$	C_2H_5OH	$\mathit{CH_3C_4CN}$	
$\mathbf{CH^+}$	$\mathbf{NH_2}$	H_2CO	CH_2NH	$\mathit{C_2H_4}$	CH_3CHO	$\mathit{H_2C_6}$	C_2H_5CN		
$\mathbf{NH}$	H_2O	H_2CS	$\mathit{H_2C_3}$	CH_3CN	$\mathit{c\text{-}CH_2OCH_2}$	$\mathbf{C_7H}$	$\mathit{CH_3C_4H}$		N = 13
$\mathbf{OH}$	H_2S	$\mathbf{C_3H}$	$\mathbf{c\text{-}C_3H_2}$	CH_3NC	$\mathit{CH_2CHCN}$	$HOCH_2CHO$	$\mathbf{C_8H}$		
HF	$\mathbf{C_2H}$	HCCH	$\mathbf{CH_2CN}$	$\mathit{HC_2CHO}$			$\mathit{HC_6CN}$		$\mathit{HC_{10}CN}$
$\mathbf{C_2}$	HCN	$HCNH^+$	NH_2CN	NH_2CHO					
$\mathbf{CN}$	HNC	$\mathbf{H_2CN}$	$\mathit{CH_2CO}$	HC_3NH^+					
CO	$\mathbf{HCO}$	$\mathbf{c\text{-}C_3H}$	$HCOOH$	$\mathit{H_2C_4}$					
$\mathbf{CSi}$	HCO^+	$\mathbf{HCCN}$	$\mathbf{C_4H}$	$\mathbf{C_5H}$					
$\mathbf{CP}$	HOC^+	$HNCO$	$\mathit{HC_2CN}$	$\mathbf{C_5N}$					
$\mathbf{NO}$	HN_2^+	$HOCO^+$	$\mathit{HC_2NC}$	$\mathbf{C_5O}$					
$\mathbf{NS}$	HNO	$HNCS$	$\mathbf{C_4Si}$	$\mathbf{C_5S}$					
$\mathbf{SO}$	HCS^+	$\mathbf{C_2CN}$	$\mathbf{C_5}$						
HCl	$\mathbf{C_3}$	$\mathbf{C_3O}$							
KCl	$\mathbf{C_2O}$	$\mathbf{SiC_3}$							
$AlCl$	$\mathbf{C_2S}$								
AlF	$\mathbf{SiC_2}$								
PN	OCS								
SiN	$\mathbf{MgNC}$								
SiO	$NaCN$								
SiS	SO_2								
$\mathbf{CO^+}$	N_2O								
$\mathbf{SO^+}$	$\mathbf{SiCN}$								
CS									
$\mathbf{SH}$									

[a] The columns contain molecules with different numbers (*N*) of atoms. Species listed in bold are free radicals (*i.e.* have one or more unpaired electrons), those in italic are unsaturated molecules.

these molecular clouds 'dark', as well as 'dense', does transmit mm-wave and infrared radiation. The grains perform at least two functions crucial to the occurrence of chemistry in dense, molecular ISCs. First, they block out short wavelength radiation from nearby stars, thereby preventing, or at least reducing, ionisation and dissociation. Second, they provide a catalytic surface for the transformation of atomic to molecular hydrogen: H_2 is by a factor of 10^4 the most abundant molecule present in ISCs.

There is little doubt that the chemistry that forms (and destroys) the molecules which are observed in dense ISCs actually occurs in the clouds themselves. Molecules may be formed elsewhere in the cosmos, for example in regions at higher temperatures, but they will be destroyed by unshielded stellar radiation much more rapidly than they could be transported to the clouds.[1] Consequently any attempts to model the chemistry that leads to the synthesis of these molecules need to employ chemical reactions whose rates remain rapid at the very low temperatures of the ISC environment. This requirement excludes any reaction which has a significant activation energy (E_{act}) since then the exponential term in the Arrhenius expression, $k(T) = A\exp(-E_{\mathrm{act}}/RT)$, becomes exceedingly small at very low temperatures.[5]

This point is illustrated in Fig. 2. It shows two 'Arrhenius plots' of $\log_{10} k(T)$ *versus* (1000 K/T) for the reaction CN + H_2 → HCN + H. The measured rate constants cover the range 295–768 K.[6] The first panel shows the data with the scale of the horizontal axis adjusted to cover the experimental range, but no more. The second panel shows the data on an Arrhenius plot, where the horizontal axis is extended to cover temperatures down to 20 K and the vertical axis is adjusted accordingly.[7] Two conclusions emerge: (i) in general, it will be hazardous to extrapolate such plots over the huge range of reciprocal temperature required to reach the temperatures prevalent in ISCs; and (ii) however hazardous such an extrapolation, it is clear that a reaction with as high an activation energy as that between CN radicals and H_2 ($E_{\mathrm{act}}/R \approx 2070$ K)[6] will have a vanishingly small rate constant at the temperatures of ISCs. Although CN is a common free radical in the interstellar medium and H_2 is by far the most abundant molecule, their reaction can play no part in the chemistry of dense ISCs.

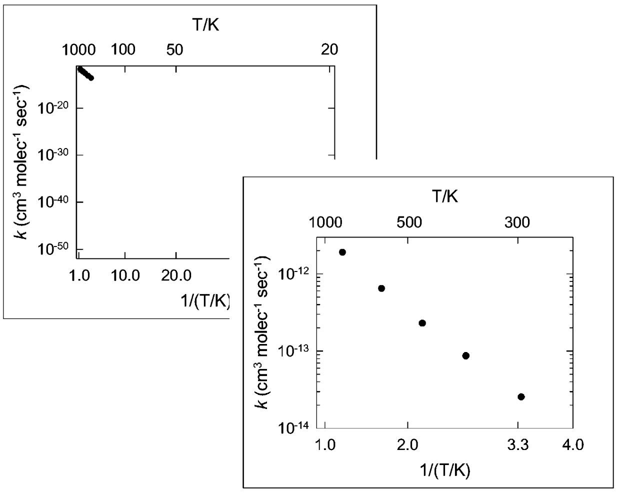


Fig. 2 Arrhenius plots of $\log_{10} k(T)$ *versus* ($1/RT$) for the reaction CN + H_2 → HCN + H on two different scales. This diagram is adapted from Fig. 2 in ref. 7, and the original data were published in ref. 6.

Clearly, for a given reaction to play a role in the chemistry of dense ISCs, it must not display 'Arrhenius behaviour'. This, in turn, means that there must be no significant energy barrier on the potential energy path leading from reagents to products. It has been known for many years that many ion–molecule reactions fall into this category. The strong attractive forces between a charged ion and the permanent or induced dipole on the co-reagent compensates for any increase in potential energy resulting from the rupture and formation of chemical bonds. The appreciation that many ion–molecule reactions are fast and that their rate constants can be estimated quite well *via* the application of the Langevin model[8] and its extensions,[9,10] has led to such reactions being dominant in models of ISC chemistry. From experimental work at higher temperatures and from theoretical considerations, there was some reason to suppose that some reactions between two neutral free radicals and between radicals and unsaturated species, such as alkenes and alkynes, might remain rapid at very low temperatures. However, it is only with the work that is reviewed in this article that it has been appreciated that rapid neutral–neutral reactions may be commoner than previously supposed, and this has led to efforts to include them appropriately in chemical models of ISCs.[11]

3 Low temperature experiments

The experiments investigating the low temperature kinetics of neutral–neutral reactions make use of a variant of the CRESU (*cinétique de réaction en écoulement supersonique uniforme*) technique first devised by Bertrand Rowe and co-workers in the 1980's to study the kinetics of ion–molecule reactions at temperatures down to 8 K.[12] The configuration of the CRESU apparatus for the study of neutral–neutral reactions has been described elsewhere.[13,14] There are now two such apparatuses, one at the University of Rennes in France and the other at the University of Birmingham. The work that I review here has been the result of a close and enjoyable collaboration between our two groups over the last 10 years.

The heart of a CRESU apparatus is an axisymmetric, converging–diverging Laval nozzle. Expansion of a gas mixture, of which the overwhelming component is the chemically inert carrier gas (Ar, N_2 or He), through a Laval nozzle generates a supersonic flow of relatively dense (*ca.* 10^{16}–10^{17} molecule cm^{-3}) gas that remains uniform for some tens of centimetres. Each nozzle is designed to produce, for a given carrier gas, a selected density and temperature that are related to the temperature and pressure in the gas reservoir that feeds the nozzle, the Mach number in the flow, and the ratio of specific heats of the carrier gas. The integrity of the flow is maintained for additions of $\leqslant$1–2% of other gases, and high levels of supersaturation can be achieved because the gas encounters no surfaces and homogenous dimerisation and condensation is generally quite slow.

In the original CRESU experiments of Rowe and co-workers,[12] the equipment was used in a flow tube mode; that is, kinetic information was obtained by measuring changes in the concentrations of reagent ions as the distance between the points at which they were formed and observed was varied. Since then, the two CRESU apparatuses have been used to examine the low temperature kinetics of a wide variety of molecular processes: ion–molecule reactions, neutral–neutral reactions, the formation of weakly bound dimers, energy transfer processes involving diatomic and large molecules, and electron attachment. (Further details are given in a recent article by Smith and Rowe.[15])

Here the focus is entirely on the kinetics of reactions between neutral species. Table 2 summarises the measurements that have been made on such reactions, giving the lowest temperature at which rate constants have been measured for each reaction between the molecular or atomic free radicals listed in the top row of the table and the co-reagent species listed in the first column. It should be emphasised that all the reactions for which there is an entry are *fast*. Because of the speed of the gas flow, and the fact that only limited amounts of co-reagent can be

Table 2 Lowest temperatures (*T*/K) at which rate constants have been measured for neutral–neutral reactions

Co-reagent	CN	OH	C_2H	CH^a		$C(^3P)^b$		Al	Si
				$v = 0$	$v = 1$	(a)	(b)		
CH_4	—	—	—	23	—	—	—	—	—
C_2H_6	25	—	—	23	—	—	—	—	—
NH_3	25	—	—	23	23	—	—	—	—
H_2	—	—	—	53	23	—	—	—	—
D_2	—	—	—	—	—	—	—	—	—
HBr	—	23	—	—	—	—	—	—	—
N_2	—	—	—	53	23	—	—	—	—
CO	—	—	—	53	23	—	—	—	—
C_2H_2	25	—	15	23	—	15	15	—	15
C_2H_4	25	—	15	23	—	15	15	—	15
C_3H_6	—	—	15	—	—	25	—	—	—
$CH_3C{\equiv}CH$	15	—	63	—	—	—	15	—	—
$H_2C{=}C{=}CH_2$	15	—	63	—	—	—	15	—	—
Butenes	—	23	—	23	—	—	—	—	—
Benzene	—	—	—	25	—	—	—	—	—
NO	—	23	—	13	—	—	15	—	15
O_2	13	—	15	13	—	15	15	23	15

[a] Rate constants for CH(v = 1) include both chemical reaction and vibrational relaxation. [b] Results in column (a) are those obtained by using a chemical marker technique involving observation of chemiluminescence from NO formed in the reaction of $C(^3P)$ atoms with NO_2; results in column (b) are from the direct observation of the disappearance of $C(^3P)$ atoms by VUV-LIF as described in the text.

added if the integrity of the flow is not to be disturbed, we can generally only measure rate constants that exceed *ca.* 10^{-12} cm^3 molecule^{-1} s^{-1}. None of the measurements on neutral–neutral reactions have been made operating the CRESU apparatus in the flow tube mode. In all these experiments, reaction is initiated by creating the free radicals by photolysis of a small concentration of a suitable photochemical precursor using a fixed frequency pulsed laser. For example, CN and OH radicals have been generated by photolysis of NCNO and H_2O_2 at 532 and 266 nm, respectively. Changes in the radical concentration are then usually followed by observing their relative concentrations, using laser-induced fluorescence (LIF) excited by a pulsed tuneable dye laser. This method is illustrated below when I describe measurements on reactions of carbon atoms in their electronic ground state, $C(^3P)$.

4 Low temperature measurements on reactions of $C(^3P)$ atoms

In the early 1990's, Husain and co-workers measured room temperature rate constants for reactions of $C(^3P)$ with an extensive range of co-reagents.[16] All the reactions with unsaturated hydrocarbons were found to be fast with rate constants that exceeded 10^{-11} cm^3 molecule^{-1} s^{-1}. These observations suggested that there is no activation energy for these reactions and, therefore, that they might remain rapid at the temperatures of dense ISCs.

I have already stressed the prevalence of carbon-containing compounds among the known interstellar molecules. Elemental carbon is, of course, created, mainly in the form of atoms, in the death-throes of stars. This is the origin of all the carbon in organic compounds and in all living species, including ourselves. The reactions of carbon atoms must be the first step in the synthesis of all complex molecules and indeed complex organisms. So their reaction kinetics, particularly in the low temperature 'molecular factories' of interstellar space is of great interest.

At the University of Birmingham, we have carried out two series of measurements[17–19] on the reactions of carbon atoms in their ^3P electronic ground state. In the earlier measurements,[17] an indirect 'marker' method was used to follow the kinetics. A small concentration of NO_2 was included in each gas mixture. NO_2 reacts with $C(^3P)$ atoms and yields $NO(B^2\Pi)$ and emission from these excited NO molecules served as a suitable marker for relative concentrations of $C(^3P)$. Measurements of this kind yielded rate constants for reactions of $C(^3P)$ atoms with O_2, C_2H_2, C_2H_4 and C_3H_6 at temperatures down to 15 K.

Recently, we have performed more direct measurements on the kinetics of reactions of $C(^3P)$ atoms by observing decays of the atoms by LIF in the presence of a variety of co-reagents. In order to observe atomic carbon in this way, it is necessary to generate tuneable vacuum ultraviolet (VUV) laser radiation in order to access the $3s^3P_J$–$2p^3P_J$ resonant transition. Each of these ^3P_J states is split into three terms by spin–orbit coupling giving rise to the six allowed transitions shown in Fig. 3. To create tuneable VUV laser radiation, we have employed the two-photon resonant four-wave frequency mixing process in xenon that is represented in Fig. 4.[18,19] Radiation from one frequency-doubled dye laser tuned to 255.94 nm ($\equiv h\nu_{UV}$) excites Xe atoms by a two-photon process to its $5p^56p(^5/_2)_2$ state. Radiation from a second dye laser operating at wavelengths between 560 and 565 nm ($\equiv h\nu_{VIS}$) is fired simultaneously and generates VUV photons ($\equiv h\nu_{VUV}$) according to the equation: $h\nu_{VUV} = 2\ h\nu_{UV} - h\nu_{VIS}$. In these recent experiments, as in the earlier indirect experiments on the kinetics of $C(^3P)$ atoms, the atoms were generated by pulsed laser photolysis of C_3O_2 at 193 nm.

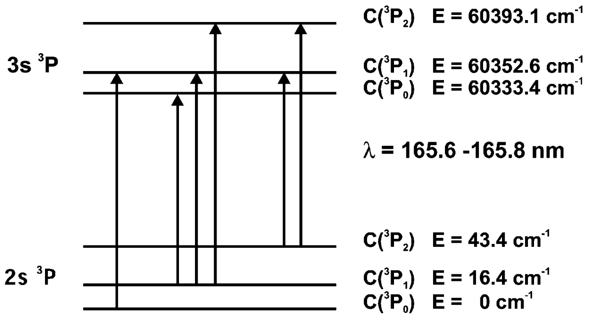


Fig. 3 Energy level diagram for the resonance transition in atomic carbon showing the allowed transitions.

One complication that may arise in low temperature experiments when radicals are generated by photolysis is that photodissociation of the radical precursor will never instantly produce radicals thermally distributed over internal states at the temperature present in the supersonic gas flow. In the case of experiments on CH radicals produced from $CHBr_3$, CH radicals are formed, and can be separately observed in the two lowest

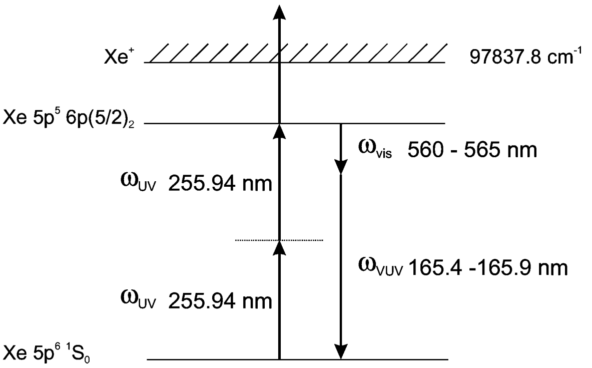


Fig. 4 Diagram showing the two-photon resonant four-wave mixing process in xenon used to generate tuneable laser radiation at *ca.* 166 nm in order to excite the resonance transition in atomic carbon.

vibrational levels, $v = 0$ and $v = 1$, of the electronic ground state. This fact has allowed the kinetics of these two states to be observed independently, yielding important information about the nature of the processes removing these radicals in collisions with different, potentially reactive, collision partners.[20] In the case of diatomic radicals, they are generally produced with a 'hot' rotational distribution, so it is necessary to wait for sufficient collisions to relax this initial distribution before starting kinetic measurements. These effects were especially marked in the case of OH radicals generated from H_2O_2.[21]

In the case of $C(^3P)$ atoms, there are, of course, no rovibrational levels to worry about, but it is necessary to consider the distribution over the $J = 2$, 1 and 0 spin–orbit components of the ^3P electronic ground state. This distribution can be observed by scanning the frequency of the VUV 'probe' radiation through the six atomic lines identified in Fig. 3. Fig. 5 shows two such LIF spectra recorded at 15 K in helium carrier, the first taken 100 ns after the pulse from the ArF excimer laser produced $C(^3P)$ atoms from C_3O_2, the second taken with a delay of 10 µs between the two laser pulses. It is clear that population is re-distributed as collisions occur with the cold carrier gas.

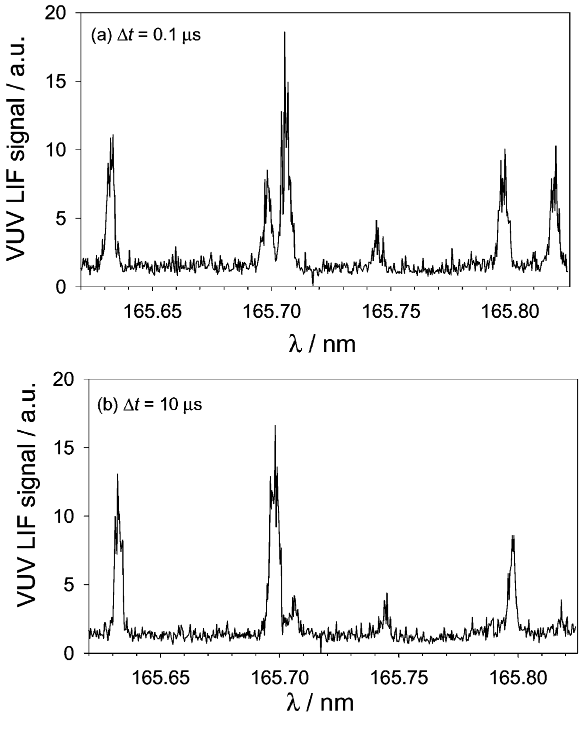


Fig. 5 Laser-induced fluorescence spectra of atomic carbon recorded in a CRESU flow at 15 K in helium but with different delays between (a) Δt = 0.1 µs, and (b) Δt = 10 µs. (Reproduced, with permission, from D. Chastaing, PhD thesis, University of Birmingham, 1999.)

The first spectrum shown in Fig. 5 is taken after only about half the carbon atoms produced have undergone a collision with a helium atom. Therefore, it essentially reflects the distribution over J that results from the photolysis process that produces $C(^3P)$ atoms and this distribution will be independent of the surrounding temperature. However, the thermally equilibrated distribution, represented at 15 K by the second spectrum in Fig. 5, will change markedly through the temperature range (15–295 K) of our experiments. At 295 K, the separations of the spin–orbit levels are small relative to k_BT and the distribution is mainly determined by the degeneracies of the J levels: $N_{J=0}:N_{J=1}:N_{J=2} = 1.00:2.77:4.04$; whereas at 15 K, the level separations are large relative to k_BT and the relative populations are changed markedly: $N_{J=0}:N_{J=1}:N_{J=2} = 1.00:0.62:0.08$.

Our kinetic measurements on the reactions of $C(^3P)$ atoms use the general method that has been employed to obtain kinetic information on the great majority of the reactions referred to in Table 2. The frequency of the 'probe' laser is fixed onto a line in the spectrum of the radical that is produced by pulsed laser photolysis of the chosen precursor. In the case of $C(^3P)$ atoms, the wavelength of the VUV laser radiation is fixed at 165.69 nm to excite carbon atoms in the $J = 1 \leftarrow J = 0$ transition. Then, in a given gas mixture, the LIF intensity is recorded as the time delay between the pulses from the photolysis laser and the probe laser is systematically varied. As shown in Fig. 6(a), after allowing time for spin–orbit relaxation, the signal decays exponentially, since the concentration of the atom is much less than that of the co-reagent, [Reag], and therefore undergoes pseudo-first-order kinetics. Experiments are repeated at a range of co-reagent concentrations and, as shown in Fig. 6(b), the second-order rate constant for the reaction under study is deduced from the variation of the pseudo-first-order rate constant with [Reag].

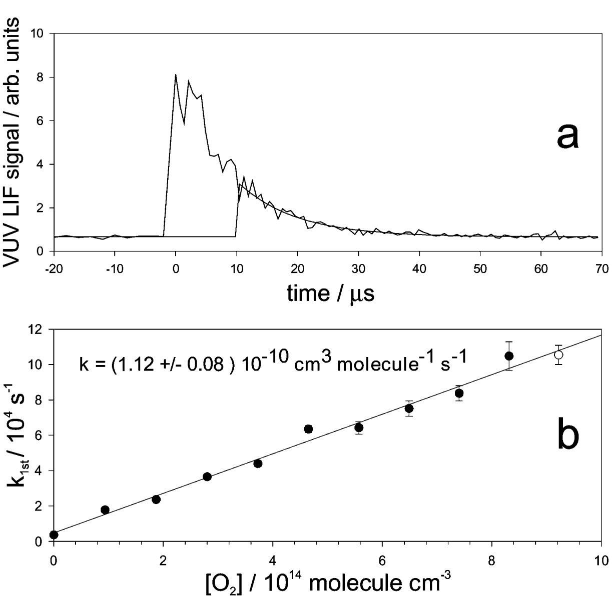


Fig. 6 Kinetic data on the reaction of $C(^3P)$ atoms with O_2 at 15 K. Panel (a) shows the decay in the VUV LIF signal from $C(^3P)$ atoms in the presence of 9.2×10^{14} molecule cm^{-3} of O_2 at 15 K. The decay is fitted to an exponential after a 10 µs delay to allow for relaxation among the spin–orbit levels of the ^3P_J ground state of the carbon atoms. Panel (b) shows the variation of the first-order constants obtained at 15 K from experiments like that in (a) with the concentration of O_2. The open point shows the value derived from the decay shown in (a). The slope of the line yields the second-order rate constant given in the diagram. (Reproduced, with permission, from D. Chastaing, PhD thesis, University of Birmingham, 1999.)

In this manner, we have determined rate constants for the reactions of $C(^3P)$ atoms with O_2, NO, C_2H_2, C_2H_4, $CH_3C{\equiv}CH$ and $H_2C{=}C{=}CH_2$.[18,19] In Fig. 7, I show the rate constants for the

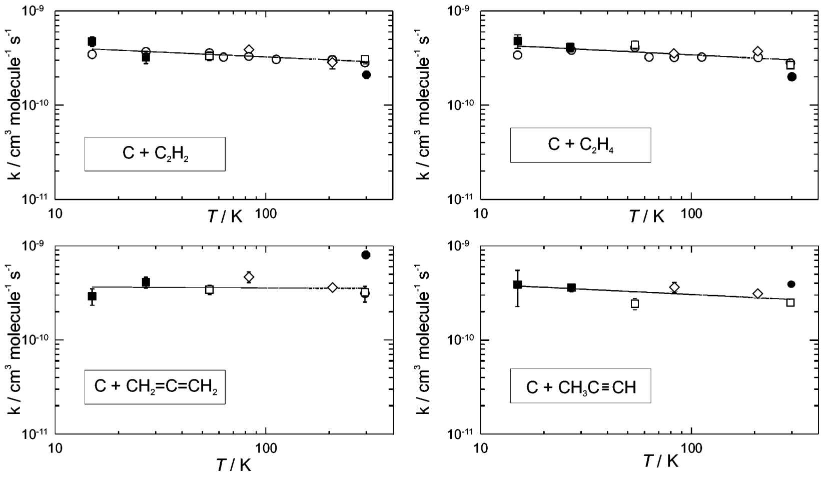


Fig. 7 Low temperature rate constants obtained in the Birmingham CRESU apparatus for the reactions of $C(^3P)$ atoms with C_2H_2, C_2H_4, $CH_3C{\equiv}CH$, and $H_2C{=}C{=}CH_2$.[19] Open circles (○) represent the data obtained earlier by the indirect marker technique.[17] Data obtained in the Birmingham CRESU apparatus with different carrier gases: He (■), Ar (□), N_2 (◇). The black circles (●) represent the room temperature data from Husain and co-workers.[16] (Adapted, with permission, from the PhD thesis of D. Chastaing, University of Birmingham.)

reactions with the unsaturated hydrocarbons. It can be seen that they show little dependence on temperature; the rate constants are close to the 'collision-determined limit' at all temperatures. One conclusion that can be drawn from this observation is that the reactivity is high for all spin–orbit states of the $C(^3P)$ atom. If this were not so, we should expect to see a stronger temperature-dependence, given the marked change in J-level populations that occurs over the temperature range of our experiments. A second conclusion is that the reactions of $C(^3P)$ with unsaturated hydrocarbons (and no doubt other species) should be included in chemical models of ISCs.

One limitation in all the CRESU experiments so far is that no evidence has been obtained about the products of any reaction. The rate constants have been determined from measurements of the disappearance of the radical species. Clearly to complete our understanding of particular reactions, not to mention the need for modelling purposes, it is desirable to identify the reaction products. In this respect, *ab initio*, quantum chemical calculations can be valuable.[22]

In general, it appears that in collisions of $C(^3P)$ with unsaturated hydrocarbons, the first stage of reaction is addition to form an energised radical complex. In most cases, this probably dissociates by loss of an H atom so that the overall process can be represented by:

$$C(^3P) + C_xH_y \rightarrow C_{x+1}H_{y-1} + H$$

However, things may be more complicated in the prototypical reaction of $C(^3P)$ atoms with C_2H_2.[23] Here, the channels to l-C_3H + H and c-C_3H + H are both, at most, slightly exoergic[22] and there is experimental evidence[24,25] that the reaction branch to $C_3 + H_2$ may occur to a significant degree. I shall say something about prospects for determining reaction products and branching in the concluding section of this article.

5 The synthesis of cyanopolyynes in interstellar clouds: the reactions of CN and C_2H radicals

The reaction of $C(^3P)$ atoms may be one step in the formation of carbon-chain species in dense ISCs. A particularly clear contribution that our studies of low temperature neutral–neutral reactions has made to the understanding of the chemistry in ISCs concerns the synthesis of cyanopolyynes. These species, $H(C)_{2n}CN$, are ubiquitous in ISCs and have been observed with n as high as 5 (see Table 1). Prior to our work on neutral–neutral reactions, several schemes based on ion–molecule chemistry had been proposed for the synthesis of cyanopolyynes, but none was entirely satisfactory.

In 1993, based chiefly on the recently measured low temperature rate constants for the reactions of CN radicals with unsaturated hydrocarbons, Smith and Sims[26] suggested that the families of neutral–neutral reactions

$$CN + HC_{2n}H \rightarrow HC_{2n}CN + H$$

$$C_2H + HC_{2n}H \rightarrow HC_{2n+2}H + H$$

$$C_2H + HC_{2n}CN \rightarrow HC_{2n+2}CN + H$$

might be responsible for the formation of cyanopolyynes at the low temperatures of ISCs. They backed up their argument by pointing out (a) that the reactions of C_2H radicals with unsaturated hydrocarbons were known to be rapid at room temperature, making the presence of potential energy barriers for these reactions unlikely, and (b) that CN and C_2H radicals are *iso-electronic* and are therefore likely to exhibit similar kinetic behaviour.

Rate constants for reactions of CN radicals were the first measured for neutral–neutral reactions in CRESU experiments,[13,27] and were obtained using the pulsed photolysis, pulsed LIF method described above for reactions of $C(^3P)$ atoms. Following the suggestion that the corresponding reactions of C_2H would probably be similarly fast, rate constants for some of these reactions were measured at temperatures down to 15 K.[28] In these experiments, C_2H radicals were generated by photolysis of C_2H_2 at 193 nm with an ArF laser. C_2H radicals do not lend themselves to straightforward observation by LIF. Consequently, these kinetic measurements were made using a 'marker' technique similar to that employed in the earlier measurements[17] on reactions of $C(^3P)$ atoms. In the case of C_2H, all gas mixtures contained both C_2H_2, as the radical source, and O_2 which reacts rapidly with the radicals and, in small yield, generates excited $CH(A^2\Delta)$. The chemiluminescence from these excited species served as the marker for C_2H.

Fig. 8 compares the rate constants for two pairs of reactions: CN, C_2H + C_2H_2[27,28] and CN, C_2H + $CH_3C{\equiv}CH$.[29] The close agreement of these sets of data and those for other reactions of CN and C_2H vindicates the original proposal of Smith and Sims[26] that these reactions are likely to play an important role in the synthesis of cyanopolyynes at the low temperatures of dense ISCs. Of course, the reactions of only a limited number of unsaturated hydrocarbons have been studied in low temperature experiments. However, two pieces of evidence suggest that the reactions of large alkenes and alkynes with CN and C_2H are

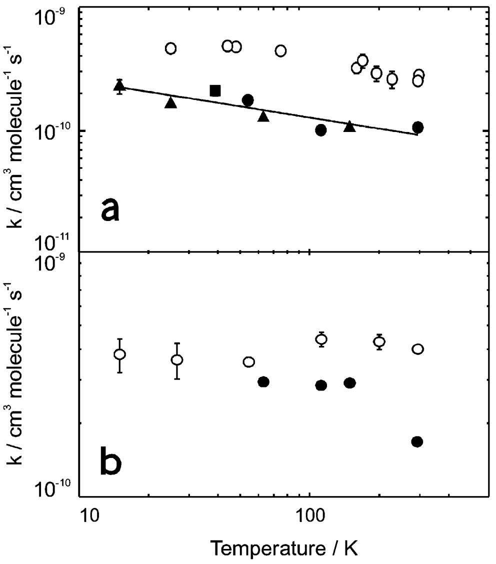


Fig. 8 Comparison of the low temperature rate constants for reaction of CN (open symbols) and C_2H (filled symbols) with (a) C_2H_2[27,28] and (b) $CH_3C{\equiv}CH$.[29]

likely to be fast at low temperatures. First, there are the large room temperature rate constants measured by Husain *et al.*[16] Second, there is the likelihood that the rates of the reactions involving a particular radical correlate with the ionisation energies of the unsaturated species: the lower the ionisation energy the more attractive the potential between the reagents. C_2H_2 has the highest ionisation energy of the alkynes and alkenes. It therefore seems clear that the reactions of alkenes and alkynes with CN and C_2H should be included in chemical models of ISCs.

As yet there have been no low temperature experiments on the reactions of cyanopolyynes. There is some evidence from modelling[30] that if these species react with CN and C_2H radicals as fast as unsaturated hydrocarbons, then the cyanopolyynes would not reach the abundances that are observed in ISCs.

6 The temperature-dependence of rapid neutral–neutral reactions

Reactions that are rapid at very low temperatures do not obey the Arrhenius equation: their rate constants are not limited by activation energies. It is therefore legitimate to ask what factors do control the magnitude and the temperature-dependence of the rate constants for these non-Arrhenius reactions. A common feature of the neutral–neutral reactions whose rates have been measured at very low temperatures is that their rate constants generally *increase* as the temperature is lowered—contrary to the situation for reactions with activation energies. However, the form of the temperature-dependence at low temperatures shows a variety of forms. In Fig. 9 is shown how the rate constants for three reactions of CN radicals vary with temperature on a log–log plot. These examples demonstrate that a variety of kinetic behaviour is found in rapid low temperature reactions.

Reactions that are rapid at the very low temperatures which are accessible in a CRESU apparatus must proceed over potential energy surfaces that have no barriers separating products from reagents. For several reactions for which low temperature kinetic data have been obtained, the absence of any energy threshold has been confirmed in molecular beam experiments that use merged beams to attain very low collision energies.[31] For most reactions whose rate constants approach the collision-determined limit at low temperatures, it is clear that the rate is determined by 'capture'; that is, by the ability of the attractive potential acting at long- and medium-range to bring the reagents into an intimate collision.

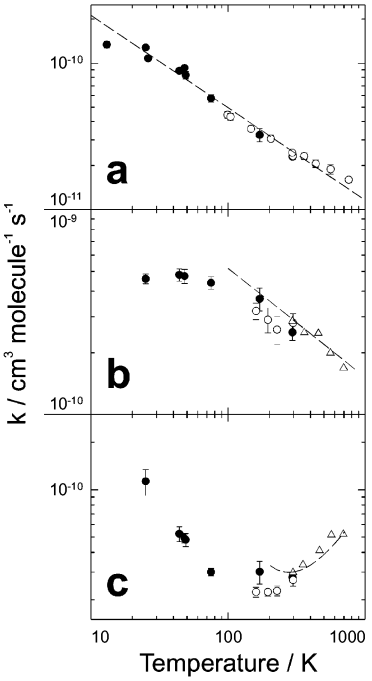


Fig. 9 Dependence of rate constants with temperature for three reactions of CN radicals: (a) CN + O_2,[13] (b) CN + C_2H_2,[27] and (c) CN + C_2H_6.[27]

As mentioned above in Section 2, the rate-determining role of 'capture' in ion–molecule reactions has been recognised for many years and capture theory is relatively easy to formulate. Thus, for the simplest case, Langevin theory considers collisions between ions and polarisable molecules and calculates cross-sections for capture and hence rate constants.[8] The cross-sections for capture (in SI units) are given by $S_{\rm reac} = \pi(2\alpha e^2/E_{\rm coll})^{1/2}/(4\pi\varepsilon_0)$, where α is the polarisability of the molecule, e is the electronic charge on the ion, ε_0 is the permittivity of vacuum and $E_{\rm coll}$ is the collision energy. Integration over a thermal distribution of collision energies yields capture rate constants equal to $\pi(4\alpha e^2/\mu)^{1/2}/(4\pi\varepsilon_0)$, where μ is the reduced mass of the collision pair. In this case, the decrease of cross-section with collision energy is exactly cancelled by the change in the distribution of collision energies with temperature making the rate constant independent of temperature.

For a number of reactions between ions and *non-polar*, but polarisable, molecules, the simple Langevin formula provides a rather accurate estimate of the rate constants and their (lack of) dependence on temperature. For a reaction between an ion and a *polar* molecule, the Langevin formula usually underestimates the rate constant, especially at low temperatures. Clary,[9] Troe[10] and their co-workers have developed similar theoretical treatments for such reactions, taking into account the additional orientation-dependent forces between an ion and a permanent dipole. The rate constants for capture then depend on the rotational state of the molecule. For higher rotational states, the rate constants decrease as the charge on the ion becomes less able to orient the molecule favourably and increase the likelihood of capture. Consequently, as the temperature is lowered and molecules increasingly populate lower rotational levels, the overall rate constant increases.

In the case of reactions between neutral species, there is no dominating long-range force. Rather the long-range forces will arise from a variety of weak 'electrostatic interactions': dispersion, induction, dipole–dipole, *etc.* Moreover, the transition state region is likely to be at short enough range for chemical forces to be operating as a new bond starts to form. All of this means that the criterion for capture is likely to vary from one chemical system to another; there is no universal formula like the Langevin formula for reaction between ions and non-polar, polarisable molecules. Nevertheless, a model based on the notion of adiabatic channels, like that for reactions between ions and polarisable molecules, provides the most promising general approach to the estimation of rate constants for rapid neutral–neutral reactions.

This approach is represented schematically in Fig. 10. Here the bold continuous curve represents the (orientation-averaged) intermolecular potential as two neutral reagents approach one another. The lighter dashed curves represent how the adiabatic potentials vary with inter-reagent separation (R_{AB}). Each of these curves correlates with a different set of initial quantum states and the adiabatic energies incorporate (a) the energy associated with centrifugal motion and (b) that associated with the chosen quantum state as the reagents approach and, for example, free rotation of a reagent becomes first hindered rotation and eventually some bending or torsional mode in the complex that results from combination of the reagents. In this model, the thermal rate constant is a weighted average of the rate constants for reaction *via* separate adiabatic channels; *i.e.*

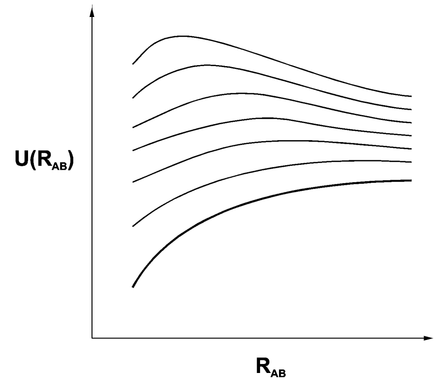


Fig. 10 Schematic diagram showing adiabatic potential energy curves for the approach of two species A and B on a monotonically attractive potential energy surface. The thick line represents the ‘bare’ electronic potential, the thinner lines adiabatic potentials each correlating with a different set of reagent states.

$$k(T) = \Sigma f_a(T)\, k_a(T)$$

where $k_a(T)$ is the thermal rate constant for reaction *via* a specific adiabatic channel and $f_a(T)$ is the Boltzmann fraction of collisions that will enter that channel at the temperature T.

In general, the individual values of $k_a(T)$ increase with T but the overall rate constant, $k(T)$, decreases with temperature because the values of $k_a(T)$ become smaller as the level of excitation increases and these high levels contain a higher fraction of the reagents as the temperature is increased. The model also predicts that the transition state region moves to smaller R_{AB} as the temperature increases and thus becomes more susceptible to the form of the chemical part of the potential at medium-range. The reason that the temperature-dependence of $k(T)$ varies from system to system is that the attractive potential acting between the reagents is different from system to system. In the limit of low collision energy and low temperature, it is expected that the long-range potential, which varies as R_{AB}^{-6}, will become dominant. In this case, simple classical arguments would lead one to expect that the capture cross-section will vary as $E^{-1/3}$ and that the rate constant for capture will depend on $T^{1/6}$. For some reactions studied by the CRESU technique, there is some evidence that, at the very lowest temperatures, the rate constants do start to fall slightly as the temperature is lowered.

I have touched on another aspect of the temperature-dependence of rates in the earlier description of reactions of C(^{3}P) atoms. I pointed out that the rate constants for the reactions of these atoms with unsaturated hydrocarbons show only a mild dependence on temperature, despite the dramatic change in spin–orbit populations that occurs across the temperature range of the experiments. It therefore seems that there is no strong dependence of reaction rates on J level. Similar conclusions can be drawn for reactions of other radicals that exhibit spin–orbit splitting. On the other hand, reactions between two radicals (*i.e.*, between an unstable radical listed in the top row of Table 2 and NO or O_2) are significantly below the collision-determined limit in contrast to most of the reactions with unsaturated hydrocarbons. The probable reason for this is that several PESs of differing multiplicity are created when two radicals (both with $S > 0$) are brought together and collisions on only some of these surfaces can lead to reaction. For example, the interaction of CN ($X^2\Sigma^+$) and O_2($X^3\Sigma_g^-$) yields a doublet ($S = \frac{1}{2}$) and a quartet ($S =$) surface. The latter surface is probably repulsive and will not therefore lead to reaction at low temperatures. Consequently, the rate constant for capture and reaction on the doublet PES has to be reduced by a factor of three to allow for the non-reactive collisions that occur on the quartet PES.

7 Summary and prognosis

The Liversidge Lecturer is asked not only to describe new knowledge but also to ‘point out the direction in which further research is desirable’. I wish to address this second requirement by reviewing the strengths and weaknesses of the CRESU technique and how some of the latter might be overcome.

On the positive side, the CRESU technique is, at present, essentially the *only* experimental method that can fairly routinely be applied to the measurement of rate constants for neutral–neutral reactions at very low temperatures, as well those for a variety of other molecular processes.[15] The lowest temperature that has been achieved in the experiments on neutral–neutral reactions, without cooling of the gases in the reservoir prior to expansion through the Laval nozzle, is 15 K. Temperatures as low as 7 K have been achieved by pre-cooling the reservoir in which gases mix before expanding through the Laval nozzle.[14] However, there are then restrictions to the systems on which measurements can be made, as vital components of the gas mixture may freeze out in the reservoir or form dimers and higher oligomers as the gas expands and cools. Evidence for the onset of dimerisation of the co-reagent molecules has been seen in some kinetics experiments at temperatures higher than 7 K (see, for example, ref. 13). Such problems will get worse at lower temperatures. Of course, this effect also offers an opportunity: to measure rate constants for the formation of weakly bound dimers. The first such experiments, on the formation of benzene dimers at temperatures at and below 88 K, were performed in the Rennes CRESU apparatus.[32]

It would appear that the measurement of rate constants for reactions below 10 K may need a radically new apparatus from the continuous flow CRESU apparatus of the type available in Birmingham and Rennes. Mark Smith and co-workers have carried out experiments on the vibrational relaxation of NO$^+$ by He in a free jet expansion at temperatures close to 1 K.[33] However, the extraction of rate constants from such measurements requires a good deal of modelling, since the flow downstream from the nozzle is highly inhomogeneous in density and temperature.

A major advantage of the CRESU method is that the density in the supersonic flow is sufficiently large that collisions are frequent and a defined temperature is established. Of course, the radicals created in the photolysis of a precursor will be generated with a distribution over internal states that is non-Boltzmann and it certainly will not correspond to the temperature of the surrounding gas. Some number of collisions will be needed to bring the distribution into thermal equilibrium. An example was given above in the case of C(^{3}P) atoms formed in the photolysis of C_3O_2. Rotational distributions of molecular radicals will also be cooled quickly by collisions with the carrier gas. This is generally not so for vibrational excitation. In the case of CH, use has been made of this fact by observing the kinetics of CH($X^2\Pi$, $v = 0$) and CH($X^2\Pi$, $v = 1$) independently. In the latter case, the overall rate of disappearance is the sum of the rates for reaction and relaxation.

A serious problem with continuous CRESU apparatuses, which may contribute to the rarity of their deployment, is the very large gas flows involved. Exceptionally large pumping capacities are required to remove the gas that propagates out of a Laval nozzle and through the reaction chamber. In the Birmingham CRESU apparatus, the total gas flows correspond to about 50 standard cubic decimetres per minute.[14] This is not just a technological or space problem. Although the bulk of the gas is the carrier, N_2, Ar or He, a significantly large flow of the co-reagent is required. Of the order of 1% of the gas flow must be co-reagent if the rate of the reaction is going to compete with physical removal. This means that it is difficult to contemplate experiments on reactions involving co-reagents that have to be synthesised, rather than bought, or with co-reagents that have a limited vapour pressure at room temperature.

A way round this difficulty may be to use pulsed Laval nozzles. Originally developed by Mark Smith,[34] they appreciably reduce the gas throughput and hence the pumping capacity that is required. Leone and co-workers have recently reported a number of kinetic studies of reactions of the OH[35] and C_2H radicals.[36] They find good agreement with the rate constants previously measured in continuous CRESU apparatuses. As yet these experiments have only provided temperatures of *ca.* 100 K, but there seems no fundamental reason why lower temperatures should not be achieved and it should be possible to measure the rates of reactions with a wider range of co-reagents.

A limitation of the CRESU apparatus, which is shared by the pulsed Laval nozzle experiment, is the inability to measure the rates of reaction between two unstable radicals (*i.e.* not NO, NO_2 or O_2). Such reactions are likely to be fast at very low temperatures and to play an important role in the chemistry of ISCs. An experimental approach that may work in a limited number of cases is to generate both radicals by photolysis. However, this will require a photochemical precursor for one of the radicals (that chosen to be in excess), which is capable of producing not only large radical concentrations but also large radical concentrations that can be measured or calculated. This approach is being pursued in Birmingham at the present time.

The final limitation of the CRESU technique, at least as applied to neutral–neutral reactions, is one that it shares with most direct kinetic measurements at more easily attainable temperatures. The measured rates correspond to those for disappearance of the reagents: no information is obtained about the reaction products, nor about branching ratios into different product channels. Clearly, from the point-of-view of modelling, it can be as important to know the products of elementary reactions included in the model as to know the rate constants for overall reaction. In a limited number of cases, it is possible to identify the reaction products from thermodynamic arguments. However, for many of the reactions that might occur in ISCs multiple sets of products are possible.

Crossed molecular beam experiments, which identify product species resulting from the single collisions that occur when the two beams intersect, can provide information about branching ratios, but the collision energy in such experiments is generally much larger than those in dense ISCs.[23,37] Certainly *ab initio* quantum chemical calculations are also useful. They can provide information about the energetic accessibility of products for which there is no thermochemical data and about the presence or absence of potential energy barriers along the reaction paths leading from reagents to possible sets of products.

However, it is important that experimental methods are developed that enable product branching ratios to be determined at low temperatures. It is difficult to apply laser-induced fluorescence to such measurements. In Birmingham, we are currently exploring the use of infrared diode laser spectroscopy. This technique may also allow the kinetics of a wider range of reactions to be explored, as well as allowing different reaction products to be observed. In addition, with an apparatus employing pulsed Laval nozzles, it may be possible to observe reaction products *via* multi-photon ionisation in tandem with time-of-flight mass spectrometry.[38]

8 Acknowledgements

The work described in this article has involved teams of talented scientists in Birmingham and in Rennes both of which have benefitted from excellent technical support. The people involved are too numerous to mention all of them by name. However, I must give special credit to two people: Bertrand Rowe and Ian Sims. As made clear in this article, the concept of the CRESU method was Bertrand's. The work on processes involving neutral–neutral species has been carried out in a collaborative project that has been as enjoyable as it has been successful. Ian Sims was responsible for performing the first experiments on neutral–neutral reaction in what was then the only CRESU apparatus in the world—in Rennes. He now jointly directs the efforts on low temperature processes in Birmingham. Finally, I am grateful to Dr Delphine Chastaing for permission to reproduce some diagrams from her thesis and to Dr Peter Barnes who helped with the preparation of diagrams for this article.

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