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Reaction Kinetics at Very Low Temperatures: Laboratory Studies and Interstellar Chemistry

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ABSTRACT

Studies of gas-phase processes at temperatures down to 10 K have recently blossomed, largely through application of the CRESU (cinétique de réaction en écoulement supersonique uniforme) technique. The results are of considerable relevance to the synthesis of molecules in dense interstellar clouds, demonstrating that the models developed to explain the observed molecular abundances must be expanded to include reactions between electrically neutral species. In addition, the experimental results have stimulated theoretical efforts to describe the factors that control the rates of such low-temperature reactions. In this Account, the CRESU method is described and the relevance of the results discussed.

The study of chemical reactions in the gas phase provides a perfect example of how science advances under influences that may, at first sight, seem contradictory. On one hand, there is the search for fundamental understanding. On the other, there is the wish or need to contribute to a broader field of scientific or technological endeavor. In

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addition, of course, progress is dependent on the development of the necessary experimental tools.

These interwoven threads can be discerned in the evolution of gas-phase kinetics. About 40 years ago, techniques became available (e.g., pulsed photolysis, discharge-flow, flowing afterglows) which allowed elementary chemical reactions to be studied in isolation and their rates under thermally equilibrated conditions to be measured reliably. Initially such experiments on chemical reaction rates were largely confined to ambient temperature and a limited range above. Kineticists certainly realized that greater understanding would be obtained by performing studies over a range of temperatures—and, of course, this desire to know more about the factors which control chemical reactivity stimulated the whole area of reaction dynamics. In addition, as the experimental capability grew, there was a demand for kinetic data to understand complex reacting environments at other temperatures. For example, an explosion of interest in the chemistry of the Earth's upper atmosphere, which started about 20 years ago, led experimentalists to adapt their equipment to study the kinetics of gas-phase reactions at temperatures down to about 200 K.

Only in the past few years have measurements been extended to even lower temperatures, and it is this work which is the subject of this Account. This research has been stimulated by three main factors: (a) the challenge of examining gas-phase reactions under conditions which had previously been unattainable, and with some of the species present at partial pressures well above their saturated vapor pressure; (b) the belief that the results of such studies would challenge our theoretical understanding of the factors which determine reactivity; and (c) the desire to understand the chemistry which leads to molecular synthesis in dense interstellar clouds (ISCs), where the temperatures are between 10 and 50 K.

Of course, it is reasonable to ask whether chemistry survives at such extreme temperatures. All students of chemistry meet the Arrhenius expression at an early stage

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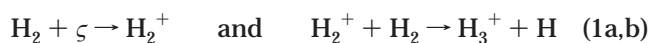
of their first course on chemical kinetics. It hypothesizes that the rate constant (k) for a chemical reaction depends on temperature (T) according to the equation $k(T) = A \exp(-E_{\text{act}}/RT)$. Clearly, if this equation always held true and if the activation energy, E_{act} , was positive, then all rate constants would approach vanishingly small values at low temperatures.

That this is not the case has been known (or at least suspected) for many years with respect to reactions between ions and neutral species. The reason is that any energy barrier associated with reorganizing the chemical bonds is more than compensated by the electrostatic attraction between the overall electric charge on the ion and the actual or induced nonsymmetric distribution of charge on the neutral species. Under these circumstances, the fundamental explanation of the Arrhenius expression—that the activation energy is a reflection of a barrier on the minimum energy path leading from reagents to products—no longer holds. One of the successes of the work that is summarized here is to show not only that this is the situation for many ion–molecule reactions but also that the reaction paths for many bimolecular reactions between neutral species have no barrier.

Chemistry in the Interstellar Medium¹

About 120 interstellar molecules have now been identified, and the list continues to grow. The molecules range in size from diatomics to the cyanopolyne $\text{H}(\text{C}_2)_5\text{CN}$ and include ions (e.g., CO^+ , HCO^+ , and HOCO^+) as well as electrically neutral species. Most of these species have been identified by using ground-based “radio-telescopes” to observe their rotational lines emitted from dark, dense molecular clouds, where H_2 and He constitute about 99.9% of the gas-phase matter, the total density is typically 10^4 molecules cm^{-3} , and the temperature is in the range 10–50 K. In these ISCs, molecules are shielded from short-wavelength stellar radiation by interstellar dust, thereby preventing their photodissociation and photoionization. Dust grains also play the crucial role of catalyzing the formation of H_2 from H atoms. The information from mmwave spectroscopy is now being supplemented by data from space-based infrared spectrometers. Observations of the warmer regions of ISCs are particularly important since this is where molecules and dust begin to assemble under the influence of gravity to form young stars.

To understand the presence and abundance of interstellar molecules is a formidable task. There is clearly a rich chemistry within the ISCs, and it is therefore necessary to propose networks of reactions that can occur at extremely low densities and temperatures. The foundation for this effort was laid by Herbst and Klemperer in 1973.² Recognizing that many ion–molecule reactions remain rapid to very low temperatures, their model was based on ion–molecule chemistry. It was proposed that cosmic rays (ζ) ionized H_2 and He, and that much of the chemistry was then initiated by the rapid conversion of H_2^+ to H_3^+ :



Because the proton affinity of H_2 is relatively low, H_3^+ is capable of protonating most atomic and molecular species with which it comes into contact. For example, H_3^+ reacts with CO to form HCO^+ . Although the part of the mechanism represented by eq 1 has been widely accepted, it is only recently that the H_3^+ ion has been observed in ISCs.³

At the time of Herbst and Klemperer’s inspirational work, there were virtually no laboratory measurements at the temperatures of ISCs, and the chemical models had to rely on estimates of the rate constants for any reactions that were included in the model. For ion–molecule reactions, such estimates could be made with a fair degree of confidence, since, for many such reactions, the simple Langevin capture model,⁴ or a modification of it,⁵ was adequate. Predicting the rate constants for reactions between neutral species is more difficult. Although it was appreciated that reactions between free radicals might be “barrierless” and therefore be rapid at low temperatures, it was often assumed that their rate constants would depend on $T^{1/2}$, as predicted by simple collision theory. It is now apparent that the rates of rapid neutral–neutral reactions usually *increase* as the temperature is lowered, since they also depend on capture by the long-range, attractive part of the intermolecular potential.^{6,7} Moreover, it is now evident that these reactions play a greater role in ISC chemistry than had previously been thought.

Low-Temperature Kinetics: Experimental Methods

Two general methods allow one to cool gases to low temperatures: cryogenic cooling and expansion techniques. Cryogenic cooling suffers from the disadvantage that any gas which is present above its saturation vapor pressure will eventually condense on the refrigerated walls of the cooled vessel. Ion traps enable one to measure the rates of reactions of ions with noncondensable neutrals⁸ but have limited applicability. Here we consider only cooling methods based on expansion.

Three kinds of supersonic expansion are represented in Figure 1. In a free jet expansion, in which gas at high pressure is allowed to escape through a small orifice into a high-vacuum chamber, the cooling can be extreme, but the medium is inhomogeneous with respect to both temperature and density, making it difficult, but not impossible,⁹ to perform kinetics experiments. The insertion of a “skimmer” into the supersonic zone of a free jet expansion generates a molecular beam. *Crossed* supersonic beams are very useful in studies of collisional dynamics, but are not useful if one’s aim is to find rate constants for bimolecular reactions under thermally equilibrated conditions.

This brings us to the CRESU apparatus, which makes use of axisymmetric, converging–diverging Laval nozzles. The first CRESU experiments were performed in Meudon in 1984,¹⁰ and there are now two independent continuous-

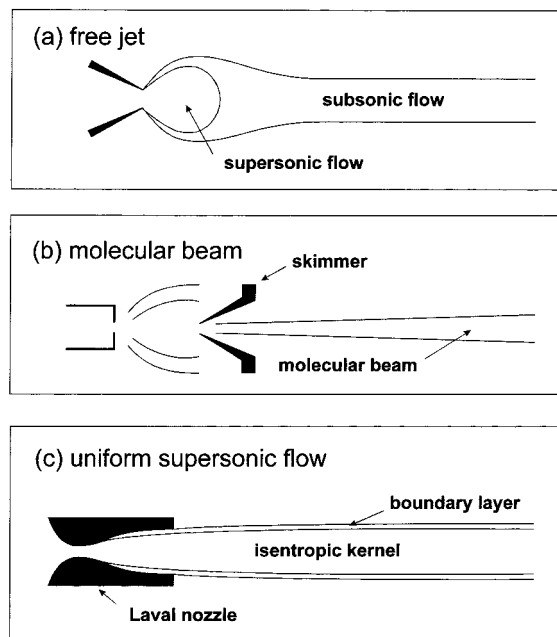


FIGURE 1. Schematic diagram of nozzles used to generate different supersonic expansions. (a) In the free jet, gas is expanded from a high-pressure reservoir through a small orifice, producing a very cold gas flow with strong gradients of density and temperature. (b) Placing a skimmer in a free jet can produce a molecular beam. (c) A uniform supersonic flow of constant density and temperature can be generated by expansion of gas from a reservoir at moderate pressure through a convergent–divergent Laval nozzle.

flow CRESU apparatuses, one in Rennes¹¹ and the other in Birmingham.¹² Here we briefly summarize the advantages and limitations of the CRESU method.

Expansion of a gas through an appropriately designed Laval nozzle provides a uniform supersonic flow of relatively dense (ca. 10^{16} – 10^{17} cm⁻³) gas. Each nozzle is designed to produce a selected density ($[M]$) and temperature for a given carrier gas (He, Ar, or N₂) which is related to the reservoir temperature, the Mach number in the flow, and the ratio of the specific heats of the carrier gas.^{10–12} To avoid clustering, helium is chosen as carrier for the lowest temperatures. The integrity of the flow will be maintained for additions of ≤ 1 –2% of other gases, and high levels of supersaturation can be achieved because the gas encounters no walls and homogeneous dimerization and subsequent condensation into higher aggregates is generally quite slow.

Once the impact pressure is measured along the axis of the flow, the aerodynamic equations can be used to extract $[M]$ and T in the supersonic flow. The temperature can be checked spectroscopically by comparing rotational line intensities for a molecular species included or generated in the flow.^{11,12} The lowest temperature achieved in a CRESU experiment is 7 K,¹² but this required the reservoir, where gases are mixed before passing through the nozzle, to be cooled in liquid N₂, which restricts the gases which can be included in the mixture. The lowest temperature achieved so far without such precooling is 15 K.

Use of the continuous-flow CRESU apparatus provides a versatile method for measuring rate constants, which

can be applied in two different ways. In the first, equilibrium in the mixture is perturbed photochemically by a pulsed laser which might generate free radicals¹¹ or excite molecules to a selected state.¹² Subsequent changes in population as reaction or relaxation occurs are followed, either by using a pulsed dye laser to generate laser-induced fluorescence (LIF) signals or, in some cases, by observing chemiluminescence. In the second mode, the apparatus is used as a “flow tube without walls”. Concentrations are observed at different distances downstream of the nozzle. This method was used in the first CRESU experiments, when ions were generated using an electron beam and observed mass spectrometrically.¹⁰

Of course, the CRESU method has its limitations. Because the supersonic flow remains uniform only for some tens of centimeters, which translates into 100–500 μ s, any change in concentration of an observed species must occur on this time scale. Given the limit placed on the introduction of an added gas, rate constants for any process other than those involving the carrier must exceed about 10^{-12} cm³ molecule⁻¹ s⁻¹ if they are to be measured. In addition, the large flows for the added co-reagent make it difficult to introduce sufficient concentration of any species with a low vapor pressure or one that is not readily available.

An inconvenience is that each set of conditions requires a new nozzle (although some nozzles designed for one carrier gas can be used with another with changes in the density and temperature). Moreover, the range of total gas densities is limited, making it difficult to examine the pressure dependence of association reactions, although five nozzles have been designed and used in Rennes which give five different densities of Ar at ca. 53 K.¹³ Finally, we note that the continuous-flow CRESU apparatus does consume appreciable amounts of gas when it is running and requires pumps that are unusually large. This feature has encouraged the development and use of pulsed Laval nozzles.¹⁴

Discussion of Results

Table 1 summarizes the wide variety of processes that have now been studied in CRESU experiments. For each process, we give the lowest temperature at which rates were measured. The low-temperature limit is set by one of three factors. First, a species introduced into the flow may cluster at an appreciable rate, so that its concentration becomes uncertain. For example, rate constants for the CN + O₂ reaction at 13 K had to be extracted from measurements at low additions of O₂, since at higher additions there was evidence of clustering.¹¹ Second, there is the possibility that species condense on the walls of the reservoir or the nozzle. Finally, there is the difficulty of constructing Laval nozzles with narrow throats to achieve the highest supersonic speeds and hence the greatest reduction in temperature on expansion. In this Account, we have chosen to review three topics.

(i) Rate Constants for Bimolecular Reactions. Rate constants for ion–molecule reactions have been measured

Table 1. Summary of Processes Studied in the CRESU Apparatuses

| process | reagent | minimum T/K^a | co-reagent |
|-----------------------------|--------------------|-----------------|--|
| ion–molecule reactions | | | |
| (i) bimolecular | | | |
| | O_2^+ | 20 | CH_4, CD_4 |
| | N_2^+ | 8 | O_2 |
| | He^+ | 8 | N_2, O_2, CO |
| | | 27 | $HCl, SO_2, H_2O, H_2S, NH_3, C_6F_6, c-C_6H_{12}$ |
| | N^+ | 8 | O_2, CO, CH_4, H_2 |
| | | 20 | $p-H_2, HD$ |
| | | 27 | $H_2O, NH_3, C_2H_2Cl_2, C_6F_6, c-C_6H_{12}$ |
| | | 45 | D_2 |
| | C^+ | 27 | $HCl, SO_2, H_2O, H_2S, NH_3, C_6F_6, c-C_6H_{12}$ |
| | H_3^+ | 27 | $C_2H_2Cl_2$ |
| | | 30 | $CO, N_2, CO_2, NH_3, SO_2, H_2S$ |
| | | 70 | CH_4 |
| | Ar^+ | 20 | N_2, O_2, H_2, CO |
| | Ar^{2+} | 30 | $He, Ar, H_2, O_2, N_2, CO_2$ |
| | Cl^- | 23 | CH_3Br |
| | O^+ | 23 | NO |
| (ii) association | | | |
| | C^+ | 13 | H_2 |
| | N_2^+ | 20 | N_2 |
| | O_2^+ | 20 | O_2 |
| | CH_3^+ | 20 | H_2, CO, N_2 |
| | Ar^+ | 27 | Ar |
| neutral–neutral reactions | | | |
| (i) bimolecular | | | |
| | CN | 13 | O_2 |
| | | 25 | $NH_3, C_2H_2, C_2H_4, C_2H_6$ |
| | OH | 23 | HBr |
| | CH | 13 | NO, O_2 |
| | | 23 | $C_2H_2, C_2H_4, \text{butenes}$ |
| | | 25 | NH_3, C_2H_6 |
| | C_2H | 23 | C_2H_2, C_2H_4, C_3H_6 |
| | | 25 | NH_3 |
| | $C(^3P)$ | 15 | $NO, O_2, C_2H_2, C_2H_4, C_3H_6$ |
| | $Al(^2P), Si(^3P)$ | 23 | O_2 |
| (ii) association | | | |
| | OH | 23 | $NO, \text{butenes}$ |
| | CH | 53 | H_2, N_2, CO |
| (iii) dimerization | | | |
| | C_6H_6 | 15 | C_6H_6 |
| collisional energy transfer | | | |
| | $Al(^2P_{3/2})$ | 44 | Ar |
| | $CH(v=1)$ | 53 | H_2, N_2, CO |
| | $NO(v=1)$ | 7 | NO |
| | $NO(v=3, j)$ | 7 | He |
| | | 23 | Ar, N_2 |
| electron attachment | | | |
| | toluene | 40, 112, 70 | He, Ar, N_2 |
| | electron | 48 | $SF_6, CF_3Br, CCl_2F_2, \text{anthracene}$ |

^a The lowest temperatures (T/K) at which measurements have been made for a particular process.

using the CRESU method since its inception. In the earliest experiments,¹⁰ an electron beam was directed across the supersonic gas flow just downstream from the nozzle exit. It created mostly ions and metastables of the carrier gas (i.e., He^+ and He metastables in helium, N^+ and N_2^+ from nitrogen). Other ions could be generated by addition of suitable molecular gases, but clearly there are limitations to this nonselective technique of creating ions, and the method was later extended by the addition of a selected ion source.¹⁵

Systematic studies of reactions involving molecules with no dipole, molecules with large quadrupoles,¹⁶ and polar molecules have been carried out.¹⁷ Two selected results are shown in Figure 2. The rate constants for reactions of ions with nonpolar molecules, even those with large quadrupoles, match the Langevin “capture” model⁴ remarkably well. They show insignificant dependence on T , and their values are generally close to those estimated from the simplest Langevin model, which takes no account of rotational motion in the molecule or of its polarizability depending on orientation.

For reactions of ions with polar molecules, there are

additional long-range forces arising from the interaction between the ion and the permanent dipole of the molecule. Theoretical treatments by Clary^{6,18} and Troe¹⁹ have supplanted the earlier average dipole orientation model⁵ and give excellent agreement with experiment. Clary’s rotationally averaged capture treatment calculates rate constants for individual rotational levels (j) of the neutral molecule and averages over these state-specific data to obtain the thermal rate constant, $k(T)$. His theory shows that, as T is lowered, the rate of capture increases most strongly for low j , so that much of the increase in $k(T)$ results from the change in rotational populations. Troe’s statistical adiabatic channel model (SACM) has some similarities to Clary’s treatment, in that reagent rotational levels are treated individually and adiabatically, analytical approximations being calculated for each rotationally adiabatic potential energy curve. As shown in Figure 2, both treatments match experimental data rather well.

An additional complication arises when one of the reagents has an open electronic shell. Now, more than one potential energy surface (PES) correlates with the

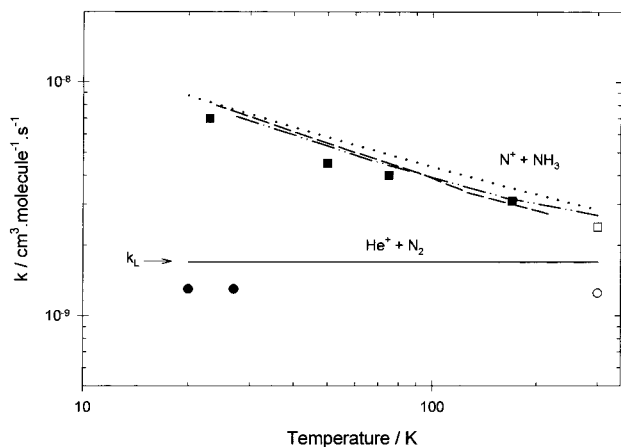


FIGURE 2. Rate constants for representative ion–molecule reactions: $\text{He}^+ + \text{N}_2$ (no molecular dipole) and $\text{N}^+ + \text{NH}_3$ (a strong molecular dipole). In both cases, the filled symbols represent data obtained in the Rennes CRESU apparatus, while the open symbols represent measurements made in selected ion flow tubes (SIFTs) or flowing afterglow experiments. The continuous line corresponds to k_L , the rate constant for $\text{He}^+ + \text{N}_2$ according to the simple Langevin model. The other lines represent the results of calculations on $\text{N}^+ + \text{NH}_3$: ($\cdot \cdot \cdot$) trajectories, ($-\cdot-$) SACM, ($- -$) adiabatic capture (ACCSA) model.

reagents, and it is not certain whether (a) all PESs will lead adiabatically and without a barrier to the products and (b) it is correct to assume electronically adiabatic collisions. If, indeed, such effects lead to differences in the rate for different fine structure states, then the observed rate constant will be less than that calculated on the basis of reaction over a single PES. Moreover, the temperature dependence of $k(T)$ will be affected by the changing populations of the fine structure states as T changes.

Nevertheless, the kinetics of ion–molecule reactions at low temperatures are quite well-understood, and theoretical methods can be used to predict low-temperature rate constants with some confidence. The situation for neutral–neutral reactions is not so clear-cut, and, as Figure 3 shows, plots of $k(T)$ versus T show various forms. A good starting point for discussion is the transition-state version of the SACM,²⁰ in which the rate constant is expressed as

$$k(T) = (k_B T/h) F_{\text{el}} (1/Q_{\text{trans}}) (Q^*/Q_A Q_B)_{\text{vib,rot}} \quad (2)$$

Q_{trans} , $Q_{\text{A,vib,rot}}$, and $Q_{\text{B,vib,rot}}$ are partition functions for the relative translational and internal motions of the reagents and F_{el} is the factor allowing for the fact that not all collisions occur on PESs without barriers which lead adiabatically from reagents to products. Q^* , the partition function of the activated complex, is given by a sum over Boltzmann terms, each involving the barrier (V_{ad}^*) on an adiabatic potential leading from reagents to products, i.e.,

$$Q^* = \sum \exp(-V_{\text{ad}}^*/k_B T) \quad (3)$$

It has been surprising to find how many *types* of neutral–neutral reaction occur rapidly at low temperatures. It was to be expected that reactions between two radicals would be fast, since then the long-range attractive

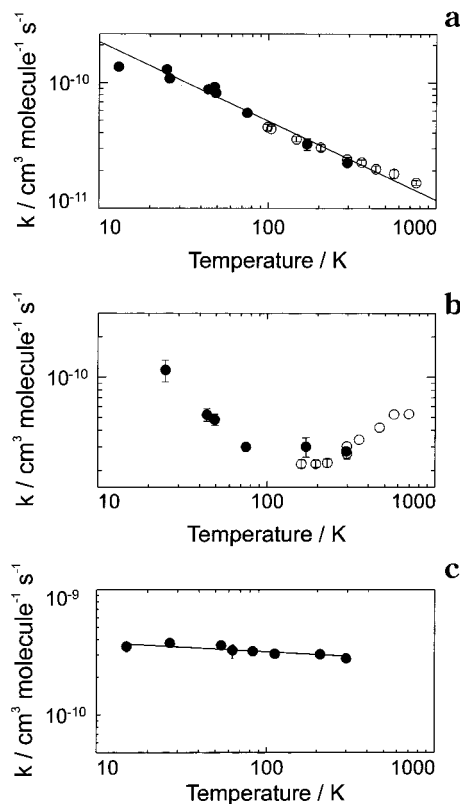
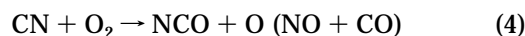


FIGURE 3. Plots showing the temperature dependence of the rate constants for three neutral–neutral reactions: (a) $\text{CN} + \text{O}_2$, (b) $\text{CN} + \text{C}_2\text{H}_6$, and (c) $\text{C}(\text{³P}) + \text{C}_2\text{H}_2$. The filled circles represent data obtained in CRESU experiments, while the open circles represent data measured in heated and cryogenically cooled cells.

potential merges into the potential arising from formation of the chemical bond as the radicals approach on the lowest PES. The radical–radical reaction



was the first neutral–neutral reaction to be studied in a CRESU experiment. $k(T)$ was shown to vary as $T^{-0.6}$ down to 13 K.¹¹

The radicals CN ,²¹ CH ,²² and C_2H^{23} and $\text{C}(\text{³P})$ ²⁴ atoms all react rapidly with simple *unsaturated* molecules such as C_2H_4 and C_2H_2 . Moreover, it has been argued that the reactions with higher alkenes and alkynes will be rapid, since such compounds have lower ionization energies than C_2H_4 and C_2H_2 .²³ At the lowest temperatures, all of these reactions approach the rates expected on the basis of capture by the long-range potentials, certainly if allowance is made for nonreactive collisions on potentials which cannot lead to products. However, if an attractive potential varying as R^{-6} , where R is the separation of the reagents, was rate-determining at all temperatures, $k(T)$ would be proportional to $T^{1/6}$, the increased rate of collisions compensating for the decrease in the cross section for capture.⁷

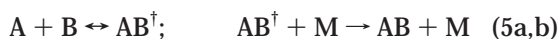
In practice, although the variation of $k(T)$ with T is different for each reaction,²⁵ the general trend is for $k(T)$ to decrease as T is raised. This can be understood in terms of eqs 2 and 3. If A and B are assumed to be structureless,

then the adiabatic maxima correspond to the centrifugal maxima on the effective potential curves for different states of orbital angular momentum, and eq 2, like a simple collision treatment, predicts that $k(T)$ is proportional to $T^{1/6}$. However, for reaction between real molecules, the adiabatic channels correlating with rotationally excited reagents tend to develop additional barriers, because free rotation becomes hindered rotation and eventually a bending vibration. As T is increased, the distributions of reagents over rotational levels changes and more collisions involve rotationally excited species. In terms of the SACM,¹⁹ a smaller fraction of the adiabatic channels are free of a barrier and there are fewer “intimate” collisions. Moreover, the maxima on these adiabatic potentials move to smaller separations where the electronic potential is no longer determined simply by the electrostatic forces, new bonds are starting to form, and possibly old bonds break. Since the form of this chemically determined part of the potential will be different for every reaction, the form of the temperature dependence of $k(T)$ varies from one system to another.

Perhaps the most surprising observation is that some reactions of radicals with *saturated* molecules are rapid at very low temperatures, implying the absence of any barrier to reaction. For example, the reaction between CH($X^2\Pi$) radicals and H_2 occurs by association; those of CN with C_2H_6 and OH with HBr apparently occur via H atom transfer. The CN + C_2H_6 reaction is especially unusual. Its rate constant has a minimum value of $2.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 200 K but increases at both higher and lower temperatures, the largest value being $1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 25 K.

The explanation for the unusual variation of $k(T)$ for CN + C_2H_6 may not be very different from that for a reaction where $k(T)$ decreases monotonically as T is raised. Once again, at higher temperatures maxima appear on the adiabatic potentials correlating with states in the reagents which have significant population. However, in this case the underlying electronic potential may not decrease monotonically as the reagents approach. At large separation, the long-range “electrostatic” forces cause the electronic potential to decrease as the reagents approach. However, when they reach separations where *chemical* interaction begins to occur, rather than the electronic potential continuing to decrease, it may even increase slightly as are bonds made and broken. Under these circumstances, it is reasonable to suppose that capture by the long-range potential determines the rate at very low temperature, but that passage through the “tighter” transition state controls the rate constant at high temperatures.

(ii) Association Reactions. Under most laboratory collisions, association occurs via the collisional stabilization of complexes formed in binary collisions:

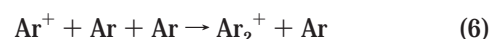


This mechanism leads to three “regimes” of behavior: (i) a *high-pressure* regime, where essentially all AB^\ddagger complexes are stabilized by collisions with M; (ii) a *low-*

pressure regime, where very few of the AB^\ddagger complexes are stabilized by collisions; and (iii) a “falloff” regime at *intermediate pressure*, where stabilization by collision and redissociation of AB^\ddagger to $A + B$ are competitive. Because rate constants show a stronger negative T -dependence in the limit of low pressure than in the limit of high pressure, the high-pressure regime is reached at lower density, [M], as the temperature is lowered. Furthermore, the high-pressure limit is reached at lower [M] for larger molecular systems. Such behavior is exemplified by the rate constants measured at $T \geq 23 \text{ K}$ ²⁶ for the addition of OH to butenes, which are in the high-pressure limit, despite the rather low density in the CRESU experiments.

CRESU studies involving smaller reagents, and therefore in the low- or intermediate-pressure regimes, are inhibited by the fact that the second-order rate constants must exceed ca. $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and are restricted by the difficulty of investigating the dependence of the rate constants on [M]. Nevertheless, it has been shown that, for the prototypical radical–radical association OH + NO, the limiting low-pressure rate constants vary as T^{-n} , where $n = 2.1$, for the range $T = 25\text{--}301 \text{ K}$.^{13a} Moreover, the CH radical has been shown to combine with three simple closed-shell molecules, H_2 , CO, and N_2 , in associations which exhibit no potential barrier.^{13b,c}

The limit on the size of second-order rate constants, which are measurable in a CRESU experiment, is relaxed if the co-reagent is also the carrier gas, a fact that has been exploited in studies on some ion–molecule associations. Notably, it has been possible to measure rate constants for



at temperatures between 27 and 141 K.²⁷ These rate constants, clearly in the low-pressure regime, bridge the gap between those measured at higher temperatures and those measured between 1 and 3 K in a free jet,⁹ and all these data are fitted well by a T^{-1} dependence. The observed T dependence is in good agreement with a simple calculation²⁸ which assumes that the recombination can be separated into the stages represented in eq 5, but the absolute values of the calculated rate constants are about 5 times smaller than those measured.

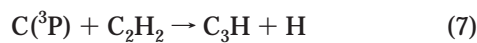
The rates of some ion–molecule association reactions depend strongly on the third-body gas. For example, the reactions of $NH_4^+ + NH_3$ and $H_3O^+ + H_2O$ are much faster in N_2 than in He, and this difference becomes stronger the lower the temperature.²⁸ A possible explanation is the occurrence of what has been called the “bound complex” mechanism. That is, rather than following the mechanism represented by eq 5 with $A = NH_4^+$ or H_3O^+ , $B = NH_3$ or H_2O , and $M = He$ or N_2 , in the presence of N_2 , NH_4^+ ions form weakly bound complexes, and these complexes then react with NH_3 molecules to yield the $NH_4^+ - NH_3$ product.

(iii) Provision of Rate Data for Modeling Interstellar Cloud Chemistry. The influence of low-temperature kinetic studies on chemical models of ISCs has been profound. For ion–molecule reactions, the CRESU mea-

measurements have largely confirmed what was expected: if the rate constants are large at room temperature, then they are at least equally large at the temperatures of dense ISCs. On the other hand, CRESU experiments on neutral–neutral reactions have unexpectedly shown that many of them may be fast at low temperatures. Given that neutral species are more abundant than ions in ISCs, it is clear that such chemistry must be included in the models.

Unfortunately, many of the neutral species observed in ISCs are free radicals which are difficult to generate and observe in the laboratory, and it is hard to see how the rates of their reactions with other radicals are going to be measured. Here is a clear and important role for theory. There is a second shortcoming of the measurements on neutral–neutral reactions: they provide no information on the reaction products. Sometimes, but not always, the products can be predicted from the thermochemistry. Nevertheless, the observation or theoretical prediction of the products of key reactions in the models is an important, and achievable, goal.

Despite the large number of reactions included in the models and the very small number for which rate constants have been measured at 10–50 K, CRESU measurements on particular reactions have made important contributions to our understanding of ISC chemistry. We cite three examples. First, there is the recent measurement²⁴ of rate constants for the reaction between C(³P) atoms and C₂H₂,



at temperatures down to 15 K, which shows the rate constant to be given by the expression $k(T) = 2.9 \times 10^{-10}(T/298)^{-0.08} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This reaction probably plays a role, and possibly a major role, in the creation of C₃H radicals, two isomeric forms of which have been detected in ISCs. Reactions of C(³P) atoms are also of fundamental interest, because the splittings of the fine structure states are comparable with $k_{\text{B}}T$ at the temperatures of the CRESU experiments, so that their relative populations change drastically between 298 and 15 K. The very mild variation of $k(T)$ suggests that all three fine structure states react at comparable rates with C₂H₂.

An important question in ISC chemistry is, “How do molecules grow?” In particular, given that a large fraction of the observed molecules are based on carbon chains, it is important to establish how these molecules are formed. Because of the low densities in ISCs, association via the mechanism represented by eq 5 is impossible. However, collisionally assisted association may be replaced by radiative association in which AB[†] complexes are stabilized by the emission of a photon:



Although it is difficult to perform experiments under conditions where radiative association dominates, the ratio of the rates of reactions 5 and 8 is given by the ratio of the rate coefficients for the two stabilization processes; i.e., ($k_{5\text{b}}/k_{8\text{b}}$). Consequently, low-temperature measure-

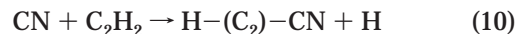
ments of collisional association, combined with calculated values of $k_{5\text{b}}$ and $k_{8\text{b}}$, lead to reasonably accurate estimates of the rates of radiative association in ISCs.

None of the species C⁺, CH₃⁺, and CH can abstract an H atom from H₂ at the temperatures found in dense ISCs because the reactions are endothermic. However, their association reactions with H₂ have all been proposed as being significant in ISCs, where H₂ is by far the most abundant species present, and the rates of the three collisionally stabilized association reactions have been measured in CRESU experiments.^{13b,15a} The creation of CH₂⁺ and CH₅⁺ in the first two of these reactions is important as it provides a route to the higher CH_{*n*}⁺ ions, and the radiative association of CH with H₂²⁹ may play a role in the formation of CH₃ radicals.

Finally, we turn to reactions that may participate in the growth of carbon chains. CRESU experiments have demonstrated that C(³P) atoms and CH and C₂H radicals all react rapidly with the simpler alkenes and alkynes at very low temperatures. Moreover, it is fairly certain that these reactions occur via initial addition followed by ejection of an H atom; for example,



Because CN radicals react in a similar fashion by replacing an H atom in alkynes, it has been suggested^{23,30} that reactions such as (9) and its CN equivalent,



may well be responsible for the synthesis, in interstellar clouds, of the cyanopolynes which are arguably the most remarkable molecular family so far identified in interstellar clouds.

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