REACTIONS BETWEEN NEUTRAL SPECIES AT LOW TEMPERATURES: LABORATORY RESULTS AND ASTROPHYSICAL MODELLING

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Abstract. Over the past few years, rate coefficients (k) have been measured for neutral-neutral reactions at low (down to 80 K) and ultra-low (down to 13 K) temperatures (T). The experimental methods and the results which have been obtained are reviewed. A surprisingly large number of reactions become faster at lower temperatures and have rate coefficients close to the collisional value below ca. 50 K. The factors which influence the form of $k(T)$ are briefly discussed and proposals are made as to how rate coefficients might be estimated for use in astrochemical models.

1. Introduction

Over the past 4-5 years, rate coefficients have been measured, for the first time, for a number of reactions between neutral species at the exceedingly low temperatures that are prevalent in dense interstellar clouds (ISCs) (Sims & Smith, 1995). This work has shown that a surprising number of such reactions are rapid — rate coefficients $\geq 10^{-10}$ cm^3 molecule^{-1} s^{-1} — under such conditions. Moreover these reactions include several reaction types, not only radical-radical reactions, which might be expected to proceed without having to surmount a potential energy barrier, but also reactions of free radicals with unsaturated and saturated molecules. As a result, it is now clear that neutral-neutral reactions may play a much more extensive role in the chemistry of ISCs than had previously been thought (Herbst et al. 1994, Bettens et al. 1994, Herbst 1995).

This paper is organised as follows. I begin by reviewing the experimental techniques that are being employed to investigate reaction kinetics below

200 K, emphasising both their strengths and limitations. After summarising the reactions which have been studied so far and giving representative examples of the variations of the rate coefficient, k, with temperature, T, some specific examples of direct interstellar relevance will be discussed in some detail. Finally, an attempt is made to provide some guidance to those modelling ISC chemistry as to how the rates and mechanisms of individual reactions might, in the absence of experimental data, be estimated without recourse to full-scale theory.

2. Experimental methods

Over the last 10-20 years the pulsed laser photolysis (PLP) - laser induced fluorescence (LIF) technique has emerged as the preferred technique for measuring rate coefficients for elementary gas-phase reactions. Two pulsed lasers are used: the first to generate a small concentration of free radicals by pulsed photolysis of an appropriate precursor (e.g. CN from NCNO) whilst the second laser is tuned to an absorption line in an electronic band system of the radical inducing it to fluoresce. The LIF signal is proportional to the concentration of the radical at the instant the 'probe' laser fires and the kinetic behaviour of the radical is observed by scanning the delay between the pulses from the two lasers.

This general PLP-LIF technique, implemented in cryogenically cooled cells or in a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus, has provided the great majority of the kinetic data which are reviewed here. It is a powerful method, especially as its intrinsic time resolution, limited by the pulse width of the photolysis and probe lasers (ca. 10 ns), and the sensitivity with which the radicals can be observed means that the effects of side and secondary reactions can be eliminated (Smith 1980). Nevertheless, it has limitations. Clearly, it must be possible to generate the radical of interest and the quantum yield for fluorescence, although it need not be unity, should be significant. Moreover application of the method is much more problematical when the co-reagent (i.e., the species reacting with the radical whose concentration is being observed) cannot simply be withdrawn from a gas bottle. Finally, although precise and accurate rate coefficients can be obtained, they refer to the reactive loss of the radical. In the standard PLP–LIF experiment, no information is obtained about the reaction products. Frequently, their nature can be *inferred* (see below) but direct measurements which relate different product concentrations, or specific product concentrations to reagent loss, are difficult and are entirely lacking from the kinetic experiments that have been undertaken so far at $T < 200$ K.

Reaction rate data at temperatures down to ca. 200 K have been needed

for models of the earth's stratosphere (Atkinson et al. 1992). In response, the PLP–LIF technique has been applied in cryogenically cooled cells and then this technique has been extended to still lower temperatures. The method is limited by the need to avoid condensation of reagents on the walls of the reaction cell but freezing-out of the radical precursor can be controlled by careful choice of the gas flow through the cooled cell — slow enough for cooling but fast enough to minimise diffusion of species to the vessel walls and their removal there (Sims & Smith 1988, Sharkey & Smith 1993, Frost et al. 1993). Some loss of the radical precursor can be tolerated, since neither its absolute concentration nor that of the radical need be known, but this is not true of the co-reagent's concentration. Consequently, the lowest temperature of such experiments is determined by the vapour pressure behaviour of the co-reagent and the kinetics of the reaction under investigation, since that will determine how much co-reagent is needed to bring about radical decay on the time-scale of the experiment. Using liquid N_2 as refrigerant, cooled cell experiments have been carried out at temperatures as low as 86 K (Frost et al. 1993).

To access still lower temperatures for studies of reactions between neutral species, special cooling techniques are required. Over the past 4 years, the PLP–LIF technique has been implemented in the super-cold environment provided in a CRESU apparatus (Sims & Smith 1995, Sims et al. 1994b). The CRESU apparatus, originally devised to study ion-molecule reactions under thermally equilibrated conditions at temperatures down to 8 K (Rowe et al. 1984, Rowe et al. 1987), has at its heart a Laval nozzle (see Fig. 2 of Sims & Smith 1995). Downstream from the nozzle a relatively dense ($n \approx 10^{16} - 10^{17}$ molecule cm^{-3}) supersonic flow of gas is generated which remains uniform for several tens of centimetres, equivalent to a few hundred microseconds. The gas is generally supersaturated but, with suitable choice of the carrier and the concentration of the co-reagent, the formation of dimers and higher clusters can be avoided (Sims et al. 1994b).

PLP–LIF experiments in cryogenically cooled cells and in a CRESU apparatus have some limitations in common but are also, in some respects, complementary. The strengths and weaknesses of the two methods are summarised in Table 1. The great strength of the CRESU technique is that it enables rate coefficients to be determined at temperatures which no other method for neutral-neutral reactions can reach. However, as yet it has not proved possible to measure rate coefficients in the CRESU apparatus for reactions between pairs of unstable free radicals (i.e. species, other than O_2 and NO, with unpaired electrons). Such measurements have been made in cryogenically cooled cells for the reactions between N and O atoms and OH and CH (Smith & Stewart 1994, Brownsword et al. 1996c). A modification

TABLE 1. Comparison of the advantages and limitations of the techniques using cryo-genically cooled cells and a CRESU apparatus.

	cryogenic cell	CRESU apparatus
lowest temperature	ca. 80 K	13 K (with pre-cooling) 23 K (without pre-cooling)
co-reagents	limited by vapour pressure	only limit is vapour pressure at room T
total pressure	up to ca. 0.5 atmos	limited to ca. 2×10^{17} cm^{-3}
unstable radical as co-reagent	can be combined with discharge-flow for atomic co-reagents	no measurements yet
lowest k_{2nd}	$> 10^{-16}$ cm^3 s^{-1}	$> 10^{-12}$ cm^3 s^{-1}
flexibility	easy to change p and T	separate nozzle for each p, T
cost	apart from lasers, economical	very large, costly pumps are required[a]
reaction products	difficult	not yet achieved

[a] the application of a pulsed CRESU technique with much reduced pumping requirements has been described by Atkinson & Smith (1994).

of the PLP–LIF technique was employed in which atomic radicals were created by dissociating N_2 in a microwave discharge. The N atoms could either be used directly or they could be converted to O atoms via the fast and stoichiometric reaction $N + NO \rightarrow N_2 + O$. The transfer of this combined discharge-flow, pulsed photolysis technique to the CRESU apparatus will be very difficult since the much higher gas flow requires that very high discharge powers will have to be coupled to the gas to create sufficient radical atoms. An alternative way of studying reactions between unstable radicals is to generate both radicals — one in a known excess concentration — by PLP.

3. Review of results on low temperature reactions

Table 2 summarises what has been achieved so far in experiments on neutral-neutral reactions at low and ultralow temperatures, by listing the lowest temperatures at which rate coefficients have been measured. It should be noted that all the reactions for which minimum temperatures below 80 K are recorded are fast since only rapid reactions can be observed in the CRESU apparatus. Moreover, it should be noted that not only reactions between two free radicals — which might be expected to react without having to surmount a potential energy barrier — remain rapid at very low temperatures. More surprisingly, several reactions of radicals with unsaturated and saturated molecules also proceed rapidly below 50 K.
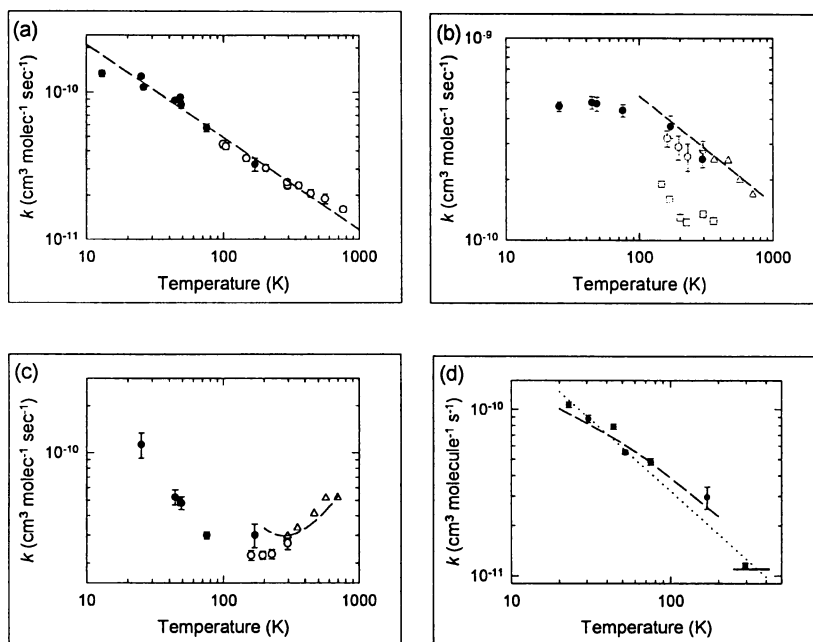
Figure 1. Temperature-dependence of rate coefficients for four neutral-neutral reactions that have been studied to very low temperatures in the CRESU apparatus: (a) CN + O_2; (b) CN + C_2H_2; (c) CN + C_2H_6; and (d) OH + HBr (adapted from Fig. 3 in Sims & Smith 1995). The square symbols in panel (b) are for the reaction between C_2H and C_2H_2 from Leone (1996).

Fig. 1 shows how the rate coefficients for a representative set of reactions vary with temperature. It is clear from these few examples that there is no common form for the variation of k with T. Although the rate constants for all the selected reactions reach their largest value at or near the lowest temperature which has been reached — and these rate coefficients are at or close to the value expected to apply to all binary collisions between the reagents[1] (Smith 1995) — the forms of $k(T)$ are different. Clearly there is no single explanation for the generally negative dependence of k on T. To examine the factors which can contribute to this variation, it is useful to examine some specific examples — chosen because of their potential relevance to the chemistry in interstellar clouds.

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[1] The rate coefficient for all collisions between two neutral species subject to a Lennard-Jones potential is only weakly dependent on temperature and has a value of ca. $(2-4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} roughly $(1/5)$th that for typical ion-molecule collisions.

TABLE 2. The minimum temperatures for which rate coefficients have been measured for reactions of CN, OH, CH and C_2H radicals. Where the temperature is given in italics the kinetics are pressure-dependent showing that the reaction responsible for removal of the radical is association.

(i) radical + saturated molecule

	CN	OH	CH	CH(v=1)	C_2H
CH_4	-	178	23	-	154
C_2H_6	25	138	23	-	153
NH_3	25	-	23	-	-
H_2	-	-	53	23	178
D_2	-	-	13	23	-
HBr	-	23	-	-	-

(ii) radical + unsaturated molecule

	CN	OH	CH	CH(v=1)	C_2H
N_2	-	-	23	23	-
CO	25	80	23	23	-
C_2H_2	25	-	23	-	143
C_2H_4	-	-	23	-	150
butenes	-	23	23	-	-

(iii) radical + radical

	CN	OH	CH	CH(v=1)	C_2H
O_2	13	-	13	-	-
NO	99	23	13	-	-
N atoms	-	103	216	-	-
O atoms	-	158	-	-	-

3.1. THE REACTIONS: CN, C_2H + C_2H_2 → C_2HCN, C_3H_2 + H

The radicals CN and C_2H are iso-electronic and might therefore be expected to exhibit comparable chemical reactivity (Sims & Smith 1993a). In concert, they might play a very important role in the synthesis of the cyano-polyacetylenes which are amongst the most remarkable molecules so far detected in interstellar clouds by mm wave spectroscopic techniques.

Reactions of the CN radical were the first to be investigated in the CRESU apparatus in Rennes (Sims et al. 1994b). The rate coefficients obtained (Sims et al. 1993b) for their reaction with C_2H_2 are shown in

Fig. 1(b). They reach an essentially constant value of ca. 4×10^{-10} cm^3 molecule^{-1} s^{-1} below ca. 80 K. It is reasonable to suppose that at these temperatures the rate of reaction is controlled by capture on the long-range potential between CN and C_2H_2 determined by dipole-quadrupole, induction and dispersion forces (Smith 1995). Moreover, from the magnitude of the rate coefficients and their lack of any dependence on total pressure, it is possible to infer that the reaction must yield $C_2HCN + H$

$$CN + C_2H_2 \rightarrow C_2HCN + H \quad ; \qquad \Delta_r H_{298}^0 = -94 \, \text{kJ mol}^{-1} \qquad (1)$$

In Fig. 1(b), rate coefficients for $C_2H + C_2H_2$ obtained in Leone's laboratory (Pedersen et al. 1993, Opansky et al. 1993, Leone, 1996) at temperatures down to 143 K are superimposed on those for $CN + C_2H_2$. In the temperature range which is common to both experiments, the two sets of data show a similar dependence on temperature. Again it is almost certain that the mechanism is one of addition followed by elimination of an H-atom:

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \quad ; \qquad \Delta_r H^0 = -135 \, \text{kJ mol}^{-1}. \qquad (2)$$

If this reaction — and those with polyacetylenes — are rapid at very low temperatures (which seems likely and which we hope to confirm), then reactions of C_2H may provide an important mechanism for carbon accretion in interstellar clouds. If a sequence of such reactions is then followed by displacement of one of the H atoms by CN, then a spectroscopically active cyano-polyacetylene is formed

$$H(C_2)_{n-1}H + C_2H \rightarrow H(C_2)_nH + H \qquad (3)$$

$$H(C_2)_nH + CN \rightarrow H(C_2)_nCN + H \qquad (4)$$
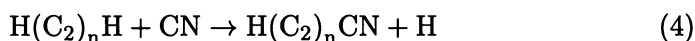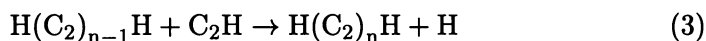
Such a sequence of reactions would appear to provide an important route for formation of cyano-polyacetylenes at the low temperatures of dense ISCs (Sims & Smith 1993a).

3.2. REACTIONS OF CN, OH, CH WITH UNSATURATED HYDROCARBONS

As the data in Table 2 show, low temperature rate coefficients have been measured for a number of reactions between the diatomic radicals CN, OH or CH and small alkenes or acetylene (Sims et al. 1993b, Sims et al. 1994b, Canosa et al. 1996). In the case of OH with butenes, the reaction proceeds by collisionally-aided stabilisation to a hydroxy-butyl radical, the reaction being in its high pressure 'saturated' limit. The reactions involving CN and CH (like that between CN and C_2H_2) probably all proceed via an energised addition adduct which then dissociates to a lower energy pair of products.
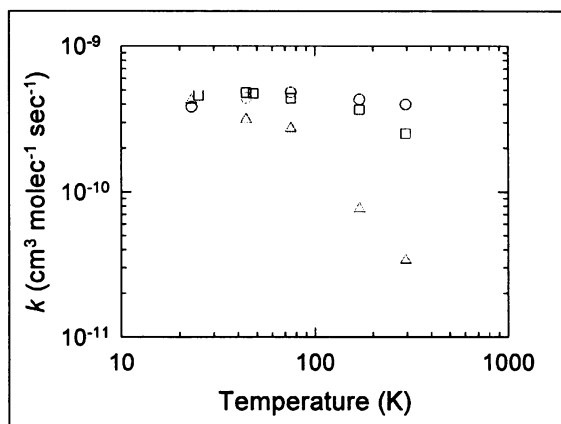
Figure 2.   Temperature-dependence of rate coefficients for three reactions between radicals and unsaturated molecules: (a) circles: $CH + C_2H_2$; (b) squares: $CN + C_2H_2$; and (c) triangles: $OH + 1$-butene.

Fig. 2 displays rate coefficients for the reactions of CN and CH with C_2H_2 (Sims et al. 1993b, Canosa et al. 1996) and for OH reacting with 1-butene (Sims et al. 1994b). For the first two reactions, the rate coefficients appear to reach an essentially limiting value of $(4-5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} below ca. 100 K, whereas the values for OH + 1-butene also appear to approach a similar limiting value but at somewhat lower temperatures. In all reactions between a quite strongly polar diatomic radical (CN = 1.47 D; OH = 1.67 D; and CH = 1.46 D) and molecules which possess large quadrupole moments and polarisabilities, the long-range forces determined by dipole-quadrupole, induction and dispersion are quite strong. It appears that at low temperatures, and not even the lowest temperatures, the rates of reaction are governed by mutual capture of the reagents on the long-range, electrostatically determined, potential in a manner analogous to that for many ion-molecule reactions (Smith 1995). In the language of transition state theory, the transition state is located in the 'loose', phase-space, limit.

The evidence is that for reactions involving polar radicals and unsaturated molecules, the rate coefficients at interstellar cloud temperatures (10-100 K) are likely to have values of $k \approx 4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. For the reactions of unsaturated molecules with non-polar radicals, including the important case of C atoms (Clary et al. 1994), the position is less clearcut, as there have been no measurements of the rate coefficients at low

temperatures. Nevertheless, it is likely that when such reactions are rapid at room temperature ($k \approx 10^{-11}$ cm^3 molecule^{-1} s^{-1}), then they will occur at or close to the collisionally determined rate below 100 K. The measurement of rate coefficients for reactions of C atoms in this temperature range is another target for future CRESU experiments.

3.3. REACTIONS BETWEEN ATOMIC AND DIATOMIC RADICALS

Reactions between radical atoms and diatomic radicals play an important role in the early stages of molecular synthesis in interstellar clouds (Herbst & Leung 1989). Unfortunately their rates are difficult to measure, although experiments have been performed down to ca. 100 K in some favourable cases (Smith & Stewart 1994, Brownsword et al. 1996c). Fig. 3 shows the rate coefficients obtained (Smith & Stewart 1994) for the reactions

$$N(^4S) + OH(X^2\Pi) \rightarrow NO(X^2\Pi) + H(^2S) \tag{5}$$

$$O(^3P) + OH(X^2\Pi) \rightarrow O_2(^3\Sigma_g^-) + H(^2S) \tag{6}$$
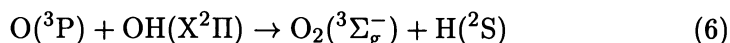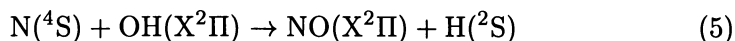
Such systems are characterised by the existence of multiple potential energy surfaces arising from the degenerate and near-degenerate fine structure states in the radical reagents (Smith 1991). As a result, part of the temperature dependence of the rate coefficients shown in Fig. 3 may arise from changes in the populations of these fine structure states and hence in the fraction of collisions which occur on the barrierless potential energy surface(s) which correlate directly with reagents and products. Reaction (6) provides an example of how account must be taken of this effect. The reagents correlate in all with 36 states ($3^4A' + 3^4A'' + 3^2A' + 3^2A''$) and the products with 6 ($^4A' + {}^2A''$) so there is a doublet surface, corresponding to the electronic ground state of HO$_2$, as well as a quartet surface across which reaction might occur. If one makes the assumption that reaction only proceeds on the lowest $^2A''$ surface then one can calculate a factor $F_{elec} = 2/g_{elec,OH}g_{elec,O}$ where the $g_{elec,i}$ are temperature-dependent electronic partition functions which can be calculated at any temperature from the known energies of the spin-orbit levels of O(^3P) and OH(X$^2\Pi$). This assumption allows one to calculate hypothetical rate coefficients, $k'(T)$, for only those collisions occurring on the ground electronic surface. They have been shown (Smith & Stewart 1994) to correlate quite well with the expression: $k'(T) = k'_{298}(T/298)^n$ and it has been suggested that the best estimate of rate coefficients for such reactions below 100 K can be made by extrapolating the values of $k'(T)$ to these temperatures and then correcting by the appropriate values of F_{elec}. For reactions (5) and (6), this leads to values of $k(T)$ of ca. $(1-2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} between 50 and 10 K.
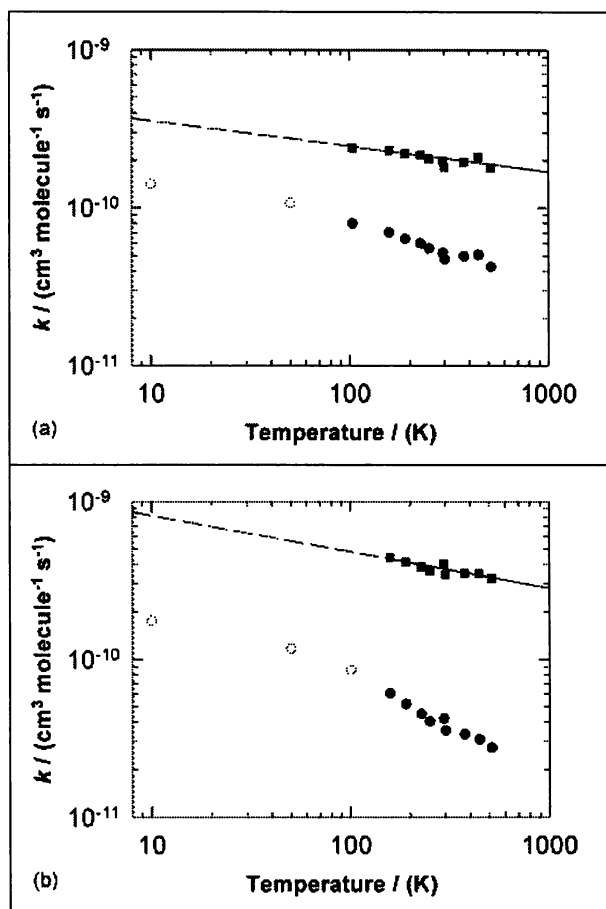
Figure 3. Rate coefficients for the reactions: (a) N + OH → NO + H and (b) O + OH → O_2 +H. The filled circles represent experimental data measured in cryogenically cooled cells. The filled squares represent the hypothetical rate coefficients for those fractions of collisions which occur on the ground state surface (see text). The lines represent the fit to these latter points and are extrapolated, as dashed lines, to very low temperatures where no experimental data are available. The open circles represent estimates of the true rate constants at temperatures at and below 100 K.

## 3.4. THE REACTION OF CH RADICALS WITH H_2

My final specific example of a reaction which is facile at low temperatures is an unusual one. Reaction between CH and the simplest saturated molecule H_2 proceeds over a potential energy surface with a deep 'well' corresponding

to formation of the CH_3 radical. At temperatures below ca. 400 K the reaction is dominated under normal laboratory conditions by collisionally-assisted association

$$CH + H_2(+M) \rightarrow CH_3(+M) \quad ; \qquad \Delta_r H^0 = -471 \text{ kJ mol}^{-1} \qquad (7)$$

In addition to kinetic studies of this reaction and its pressure dependence down to 53 K, rate coefficients have been measured for the isotope exchange between CH and D_2 and for the relaxation of CH(v=1) by H_2 and D_2 (Brownsword et al. 1996a). The results demonstrate that the formation of energised CH_3 radicals from $CH + H_2$ is rapid even at temperatures as low as 13 K.

Of course, in the thin environment of ISCs collisionally-assisted association is negligibly slow, but it can be replaced by radiative association, as has been suggested for a number of important ion-molecule reactions, notably

$$C^+ + H_2 \rightarrow CH_2^+ + h\nu \quad \text{and} \quad CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu. \qquad (8)$$
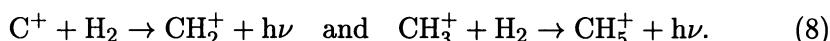
Accordingly the rate of radiative association of CH with H_2 at temperatures between 10 and 100 K have been estimated (Brownsword et al. 1996b) allowing for quantum tunnelling (Smith 1989a,b) through the centrifugal barrier associated with $CH + H_2$ collisions. Parallel calculations on collisionally-assisted association have been performed and a comparison with the experimental results for this process has been used to 'calibrate' the theoretical estimates. The results indicate that between 10 and 50 K, the rate coefficient for $CH + H_2$ association has a value $k_{RA} = (1-2) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}. The effects of tunnelling are quite large, due in part to the relatively long radiative lifetime of energised CH_3 radicals.

Although radiative association of CH with H_2 only occurs in about 1 in 10^6 collisions, its potential importance in interstellar clouds is accentuated by the high relative abundance of H_2. Nevertheless, it does not appear that this reaction will be a major loss mechanism for CH in dense clouds since other reactions, such as that between CH and atomic oxygen, are likely to be more rapid — in this case by a factor of ca. 100. However the reaction of $CH + H_2$ creates a route for formation of CH_3 which appears to compete with routes involving ion-molecule chemistry and, in particular, those involving the radiative association reactions (8) and (9).

4. Neutral-neutral reactions and chemical modelling of interstellar clouds

Although the CRESU experiments on neutral-neutral reactions at very low temperatures have been very successful, the relatively few reactions that

have been studied so far have been chosen on the criterion of being experimentally tractable rather than astrochemically important. For the foreseeable future, it will be necessary to estimate many of the rate coefficients in astrochemical models. Ideally, such estimates would be made by adiabatic capture (Clary 1988, Clary 1990) or statistical adiabatic channel models (Quack & Troe 1975, Troe 1986, 1987, 1994) based on accurate long-range potentials. Unfortunately, applying full-scale theory to all the reactions for which rate coefficients are required is unrealistic and, in any case, the necessary long-range potentials do not exist for more than a handful of reactions. Consequently, in this last section of this paper, I seek to give some cautious guidance as to how approximate estimates might be made of the required rate coefficients. For this purpose, it is again useful to categorise neutral-neutral reactions involving free radicals according to whether the co-reagent is a radical, an unsaturated molecule, or a saturated molecule.

When both reagents are radicals (i.e., have one or more unpaired electrons), there will generally be more than one potential energy surface which correlates with the separated reagents (Smith 1991) and one, or possibly more, of these surfaces will be monotonically attractive as the reagents approach. If there are products of lower potential energy than the reagents which can be reached by breaking one bond in the adduct, as in, for example, $CN + O_2 \rightarrow (NCOO) \rightarrow NCO + O$ and $O + OH \rightarrow (O_2H) \rightarrow O_2 + H$, then the reaction will be rapid and the rate coefficient will almost certainly increase as the temperature is lowered. When $T <\sim 50$ K, k will be determined by capture on those attractive potential energy surfaces which lead adiabatically to the products and a reasonable estimate of k may be made by (i) carrying out a simplistic calculation of the rate coefficient for capture based on the long-range potential determined by dispersion, induction and multipole-multipole forces, and (ii) correcting for the effects of electronic degeneracy or near-degeneracy in the radical reagents which means that only a fraction of reagent collisions will occur on the barrierless surface(s) leading to products. For the many reactions between atomic and diatomic radicals which may play a role in the chemistry of ISCs, the above procedure will lead to values of $k \approx (1 - 2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} below ~ 50 K. Often, but not always, the products of such simple reactions are clear on thermochemical grounds.

Under laboratory conditions, the reactions of free radicals with unsaturated molecules (especially alkenes and alkynes) usually proceed by initial addition to produce a radical adduct, whose fate will depend on a number of factors: e.g. the total pressure, the temperature, the size of the system, and whether the new bond formed is the weakest in the adduct. If it is, only association is possible. Collisional stabilisation will be involved in the laboratory but only radiative association can occur at the low densities in

TABLE 3. Products and enthalpies of reaction for the reactions of CH radicals with CH_4 and C_2H_2. The products listed in the second column can be reached from the initially formed adduct by cleavage of one bond; those listed in the fourth column require a more complex re-arrangement in the intermediate.

Reagent	Products	$\Delta_r H^0/\text{kJmol}^{-1}$	Products	$\Delta_r H^0/\text{kJmol}^{-1}$
CH_4	(C_2H_5)	-403		
	$C_2H_4 + H$	-250	$C_2H_3 + H_2$	-245
	$CH_3 + CH_2$	+15	$C_2H_2 + H_2 + H$	-75
			$C_2H + 2\,H_2$	+45
C_2H_2	(CH_2CCH)	-487		
	$CH_2CC + H$	-37	$CH_3 + C_2$	+154
	$CHCCH + H$	-41	$C_2H_3 + C$	+158
	$CH_2 + C_2H$	+131	$CCCH + H_2$	?
			$C_3 + H_2 + H$	+231

ISCs. Of the reactions between radicals and unsaturated molecules which we have studied, OH + butenes, CH + CO and CH + N_2 proceed by association, the remainder by addition-elimination mechanisms, as exemplified by CN + C_2H_2. Results on reactions of this last category suggest that if $k(298) > 10^{-11}$ cm^3 molecule^{-1} s^{-1} then they are uninhibited by any potential energy barrier, and their rate coefficients below 100 K are likely to exceed 10^{-10} cm^3 molecule^{-1} s^{-1}.

Addition-elimination reactions between radicals and alkenes and alkynes, as well as those between larger free radicals, may frequently proceed by more than one reaction channel and laboratory experiments may provide no guidance as to the nature of the products. To illustrate how one might be able to infer the chemical products, I consider the reactions of CH radicals with CH_4 and C_2H_2 (Canosa et al. 1996). The arguments deployed follow those of Berman et al. (Berman & Lin 1983, Berman et al. 1982). Possible reaction channels, with the corresponding enthalpies of reaction are listed in Table 3.

It appears that CH + CH_4 must react via initial formation of an energised C_2H_5 radical with ca. 153 kJ mol^{-1} more energy than C_2H_4 + H. Moreover, from measurements of the rate of addition of H atoms to C_2H_4, it is known that the threshold energy for dissociation of C_2H_5 to C_2H_4 + H is only slightly greater than the endothermicity of the process. Consequently, the energised C_2H_5 radical formed from CH + CH_4 will dissociate (probably in < 1 ps) to C_2H_4 + H and other processes will not be able to compete. It therefore seems that the reaction of CH with CH_4 should lead exclusively to C_2H_4 + H.

When CH reacts with unsaturated hydrocarbons, the most likely initial

step is again addition of CH. Products formed by fission of CC bonds are energetically less favoured and the products obtained by elimination of an H atom again seem most likely. Such arguments will not always allow one to decide unequivocally between different sets of products. For CH + C_2H_2, high quality quantum chemical calculations have been carried out. These calculations suggest that at low temperature and pressure the main products will be CH_2CC + H rather than CHCCH + H. The potential of quantum mechanical calculations for deciding between competing reaction channels has been amply illustrated in studies carried out to aid combustion modelling (e.g., Miller & Melius 1989).

The rates of reactions between radicals and saturated molecules are hardest to predict. The fact that several have been found to proceed very rapidly at low temperatures has been one of the most surprising aspects of the experiments conducted in the CRESU apparatus. Again, if a reaction is found to have a rate coefficient at room temperature in excess of 10^{-10} cm^3 molecule^{-1} s^{-1}, then it seems possible that it will proceed rapidly under the conditions in ISCs.

5. Conclusions

There is now ample evidence that many bimolecular reactions between electrically neutral species proceed at or close to the simple collisional rate at very low temperatures. Neither the venerable Arrhenius equation, $k = A \exp(-E_{act}/RT)$, nor the formula $k(T) = k(298)(T/298)^{0.5}$, which represents how the rate coefficient for hard-sphere collisions depends on temperature should be used to estimate their rate coefficients. Generally, if a rate constant for a neutral-neutral reaction has been found to exceed 10^{-11} cm^3 molecule^{-1} s^{-1} at room temperature, then there is unlikely to be an activation energy associated with the reaction. Its rate is more likely to be determined by 'capture' and its rate coefficient will probably increase to lower temperature reaching a value close to the collisionally determined value at the temperatures of dense interstellar clouds. Finally, it should be emphasised that this is an area of research which is in its infancy. Theoretical efforts, both via quantum chemistry and rate theories, as well as more experimental measurements are badly needed and are likely to be forthcoming in the next few years.

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Discussion

Langhoff: Ab initio quantum chemistry has proven to be very useful for determining mechanisms and reaction barriers. Have you made use of these techniques in your studies of neutral-neutral reactions?

Smith: I agree entirely that quantum chemical techniques are very useful in establishing the likely yields into different product channels where more than one such channel is energetically possible. We have not carried out such calculations ourselves but do use the results of others to assign likely reaction products, as in the case of $CH + C_2H_2$ referred to in my talk.

Millar: In my talk I used the word "everything" as an astronomer would use it, i.e. ion-molecule chemistry works for most things, but it is clear that there are particular species which have chemistries dominated by neutral-neutral reactions. Your work, and that of Bertrand Rowe, has demonstrated very beautifully the importance of these reactions. Since many neutral-neutral reactions are rapid at low temperatures, the determination of products becomes essential. Could you make some comments about the possibility of detecting products in the short term?

Smith: Thank you for the first part of your comment. As I indicated in my talk, the observation of reaction products and the measurement of branching ratios, i.e. the relative yields where more than one product channel is energetically accessible, is very difficult. We are attempting some such experiments at room temperature, using IR absorption techniques, but it would be difficult to interface them with the CRESU apparatus. In the short term, quantum chemical calculations may provide the best way forward by mapping out the minimum energy paths from reagents to different sets of products, as in the case of the reaction $NH_2 + NO \rightarrow N_2 + H_2O$ (see also question by Langhoff).

Ter Meulen: Do you probe the vibrational distribution of the product molecules, and what about the intial population distribution of the molecules produced by photolysis?

Smith: Let me answer the second part of your question first. Of course, it is true that the radical produced by photolysis is not initially in thermal equilibrium with the cold gas in the supersonic flow. However, we can check the internal state distribution and the rate of relaxation by scanning the frequency of the probe laser at various delay times. The kinetic measurements are begun only after the rotational relaxation and, by inference, the translational relaxation are complete.

Neither CN nor OH are produced vibrationally excited in the photolysis processes which we use. $CH(v > 0)$ is formed in significant concentrations and care has to be taken to ensure that its relaxation is either much faster or much slower than reactive loss. We have not yet measured any product state distributions at low temperatures, but do plan such experiments, initially on the NCO formed in the reaction between CN and O_2.

Herbst: What about the reactivity of O atoms and your criteria?

Smith: It is true that $O(^3P)$ atoms are generally rather unreactive compared with other atomic or small molecular free radicals. For example, the reactions in which they abstract an H-atom from alkane have rather large activation energies. Moreover, reactions initiated by O atom addition to alkenes or alkynes seem likely to be slow below 100 K. On the other hand, there seems no reason why atomic oxygen will not react rapidly with other *radicals* at low temperature (as in the case of O + OH), though allowance may have to be made for the effects of electronic degeneracy and near-degeneracy as I suggested.

Saxena: The rate of the reaction: $C_2 + O \rightarrow CO + C$ has not been determined to date. Will you be giving preference to its experimental determination in your set-up? There is an urgent need for its determination in cometary chemistry.

Smith: The reaction between atomic oxygen and C_2 involves two unstable species as reagents. As I indicated in my talk, such reactions are very difficult to study experimentally, especially in a CRESU apparatus. I am afraid that I cannot undertake to give the study of this reaction precedence in our future work.

Pecker: The literature referred to in your paper is mainly published in J. Chem. Phys. and in other chemical journals. It would be exceedingly useful to publish review papers on these questions in astronomically orientated journals. This is a request! At the present time, our access to chemistry through *WWW* networks is still very rare or/and difficult!