

RECENT ADVANCES IN THE STUDIES OF REACTION RATES RELEVANT TO INTERSTELLAR CHEMISTRY.

Nigel G. Adams and David Smith
Department of Space Research
University of Birmingham
Birmingham B15 2TT
England

ABSTRACT. The current status of laboratory measurements of the rate coefficients for ionic reactions involved in interstellar molecular synthesis is discussed and the experimental techniques used to acquire such data are briefly described. Examples are given of laboratory data which are being obtained at temperatures close to those of interstellar clouds. Particular attention is given to the results of recent theoretical and experimental work which show that the rate coefficients for the binary reactions of ions with polar molecules at low temperatures are much larger than previously assumed. It is shown how these new developments in experiment and theory are reconciling the differences between predicted and observed abundances for some interstellar molecules. Also briefly discussed are: - the phenomenon of isotope exchange in ion/neutral reactions which explains the apparent enrichment of heavy isotopes in some interstellar molecules, the role of atoms in molecular synthesis, some studies of ion/neutral reactions pertaining to shocked regions of interstellar clouds, ternary association reactions and the analogous radiative association reactions, and recent new laboratory measurements of dissociative recombination coefficients. Finally, some guidance is offered in the proper choice of critical kinetic data for use in interstellar chemical modelling and some further requirements and likely future developments are mentioned.

1 INTRODUCTION

It has been appreciated for some time that molecular synthesis in interstellar clouds (ISC) occurs mainly via many parallel and sequential gas phase binary ionic reactions (e.g. Dalgarno and Black 1976; Herbst and Klemperer 1976; Watson 1976; Smith and Adams 1981). The small positive ions formed in ionizing events, react with neutral molecules to form polyatomic ions which then recombine (dissociatively) with electrons to produce a great variety of observed interstellar molecules. Support for this scenario lies in the reasonable agreement between the observed relative abundances of many interstellar molecules and the abundances predicted by ion chemical models (e.g. Hartquist et al. 1978; Prasad and

Huntress 1980; Herbst 1983; Millar 1985). These models are based on the data obtained from many laboratory experiments, notably flowing afterglow (FA) (Ferguson et al. 1969; Albritton 1978), ion cyclotron resonance (ICR) (Huntress 1977; McIver 1978) and selected ion flow tube (SIFT) (Smith and Adams 1979, Adams and Smith 1983) experiments. The general features of interstellar chemistry are now well understood and a very large amount of laboratory data is available concerning the rate coefficients and products for relevant ion/neutral reactions (Huntress 1977; Albritton 1978; Graedel et al. 1982; Leung et al. 1984); less data are available relating to dissociative recombination (Mitchell and McGowan 1983). Most of the early data were obtained at or somewhat above room temperature and, of necessity, these had to be used in modelling the chemistry of the much-lower-temperature ISC. This undesirable, yet unavoidable approach has had a large measure of success because of the following features of ion/neutral reactions. Most ion/neutral reactions are very efficient, i.e. reaction occurs on almost every collision, and, for such reactions, the rate coefficients hardly vary with temperature. Thus, when the rate coefficient, k , for a particular reaction is measured to be equal to the collisional rate coefficient, k_C , at room temperature then it is expected to remain equal to the appropriate collisional value at much lower temperatures (Adams and Smith 1983). This principle has usually been adopted in ISC chemical models. Indeed, when laboratory values were not available for reactions included in the models then it has often been assumed that the appropriate k is the k_C value. Calculations of the k_C for ion/neutral reactions involving non-polar neutrals are simple and the k_C is predicted to be temperature independent (Gioumousis and Stevenson 1958) in agreement with experiment. For polar molecules, the procedure is not so simple and the k_C are predicted to be dependent on temperature (Su and Bowers 1979). Further insights into this have been gained very recently and we discuss this in Section 3. Of course, not all ion/neutral reactions are observed to proceed at the collisional limiting rate at room temperature, and often $k \ll k_C$. For such reactions, the k invariably changes with temperature (e.g. Adams and Smith 1983) usually unpredictably, and then it is obviously essential to measure k at low temperatures if the reaction is to be included in ion-chemical models of ISC.

Notwithstanding the large amount of kinetic data available, as more molecular species are discovered in ISC and as more sophisticated models are constructed to describe the routes to their synthesis, the need arises for more kinetic data. Also, as more accurate measurements of relative abundances are obtained and more detailed ion-chemical models are constructed, unacceptable discrepancies between observed and predicted relative abundances of specific molecules are being revealed. Suspicion then falls, to some extent, on the kinetic data used in the models which, as mentioned above, generally relate to 300 K. Thus much effort is currently being made to obtain laboratory data at appropriately low temperatures.

In this paper, we refer to the experimental techniques which are now being exploited to obtain ionic reaction rate data at low temperatures and discuss some of the exciting new data being obtained. We are mostly concerned with positive ion/neutral reactions, including some which occur in shocked regions of ISC. We stress the importance of using ion-chemical

models data which are appropriate to the specific conditions existing in the regions to be modelled. A brief summary is also presented of recent studies of some dissociative recombination reactions important in interstellar chemistry.

2 LABORATORY TECHNIQUES

The majority of the data used in the first ion-chemical models of ISC was obtained by exploiting the flowing afterglow (FA) (Albritton 1978) and particularly the ion cyclotron resonance (ICR) (Huntress 1977) techniques. These data have been discussed in detail in many review articles which have also discussed the understanding of ion chemistry which has resulted from the exploitation of these techniques. The FA data were obtained with truly thermal reactants, largely at 300 K, and can be considered to be reliable. The ICR data also relate to neutral reactant temperatures near to room temperature, but there is considerable evidence that the reactant ions in ICR cells are often suprathermal. Therefore, it must be stressed that ICR data should be used with great caution in interstellar models, especially when the measured rate coefficients, k , are significantly less than the collisional rate coefficients, k_c , since in these cases significant variations in k with temperature are to be expected. However, when $k \approx k_c$, then ICR data are generally reliable and can be a valuable indicator of the k values and of the reaction mechanisms. Clearly, for interstellar modelling it is desirable to obtain data for which the temperature conditions are exactly specified and for which the temperatures are appropriate to ISC, say between 10 and 200 K. To this end, the variable-temperature selected ion flow tube (VT-SIFT) (Smith and Adams 1979), the CRESU (Cinétique de Reaction en Ecoulement Supersonique Uniforme) experiment (Rowe et al. 1984) and the Ion Trap (IT) experiment (Walls and Dunn 1974) were developed. Each of these experiments represents an important advance, yet each has its disadvantages as well as advantages.

2.1. The VT-SIFT Technique

The first data from the VT-SIFT appeared in 1980 (Smith and Adams 1980; see also Adams and Smith 1983). It is a variant of the flowing afterglow but with additional desirable features (Smith and Adams 1979). Mass analysed ions are injected into an inert flowing gas (usually helium) in which they translationally and rotationally thermalise. Excess vibrational and electronic energy (above thermal) may remain in certain ions and this possibility must be investigated carefully in each case. Steps can be taken to minimise such excess energy, for example by control of the ion source gas pressure. Reactant gas can be added to the carrier gas/ion swarm and the reaction rate coefficients determined and the product ions identified. Presently, experiments can be carried out over the temperature range 80 to 600 K (this temperature range could be extended to some extent in both directions) and thus variations in rate coefficients and product branching ratios for binary reactions can be studied as a function of temperature. Modest extrapolations in temperature can therefore provide data appropriate to cold ISC. Ternary association reactions can also be studied over the available temperature

range and, from such studies, radiative association rate coefficients can be estimated (Smith and Adams 1977, 1978a, b; Herbst et al. 1983; Ferguson et al. 1984). Data acquisition is relatively simple and an enormous amount of reliable data has been obtained pertaining to interstellar chemistry using this technique (Smith and Adams 1978a, 1984a, 1985a; Adams and Smith 1983). There are however, two important limitations of the technique. The first is that the lowest pressure at which measurements can be made is (for many association reactions) too high for binary radiative association to be directly investigated. However, fortunately rate coefficients for radiative association can be inferred from pressure dependence studies (see Section 4). A more unfortunate limitation is that reactions involving condensable vapours (e.g. H_2O , NH_3 , CH_3OH , etc.) cannot be studied at the lower temperatures because of condensation problems (such studies are more readily possible using the CRESU technique).

2.2. The Ion Trap (IT) Technique

The first data from the IT appeared in 1981 (Luine and Dunn 1981). Ions are created and stored in a Penning-type ion trap, the walls and surfaces of which can be cooled to temperatures as low as 4 K using liquid helium. Reactant gases are added and the rate of decay of the ions is monitored. Reactant gas pressures are so low that ternary effects are never important and thus only binary reactions are studied. The trapping times of the reactant ions can be very long which allows any residual internal excitation produced during ion formation to radiatively relax. Thus the translational and internal 'temperatures' of the ions can be very low. The types of gases which can be introduced into the trap at such low temperatures are few (e.g. H_2 , CO , CH_4) and so the technique has limited application. Nevertheless, it has had some spectacular successes (which are referred to in Section 3).

2.3. The CRESU Technique

The first data appeared in 1984 (Rowe et al. 1984a). Low temperatures are created in a supersonic gas by expansion through a de Laval nozzle (Rowe et al. 1984b). Ionization is created in the cold, fast-flowing gas using a high energy electron beam. Thus a low temperature flow reactor is created in which the ions and neutrals are rapidly translationally and rotationally thermalised. However, residual vibration excitation is a potential problem. Ion/molecule reactions have been studied at temperatures down to 8 K (Marquette et al. 1985). A unique feature of the technique is that the reactions of condensable vapours can be studied below the condensation temperature by introducing them into the reactor in the warmer reservoir region prior to expansion (and cooling) of the gas. The anticipated addition of a SIFT-type ion injector to the CRESU apparatus will render it an outstandingly valuable experiment for studying ionic reactions at very low temperatures.

2.4. The VT-SIFDT Technique

The addition of an electrostatic drift tube element to the VT-SIFT has created

the even more versatile variable-temperature selected ion flow drift tube (VT-SIFDT) (Smith et al. 1984; Adams et al. 1985). With this apparatus, ion/neutral reactions can be studied not only over a wide temperature range but also as a function of ion/neutral centre-of-mass energy up to about one electron volt. This technique is now providing data relating to the chemistry occurring in the shocked regions of ISC (Adams et al. 1984).

2.5 The VT-FALP Technique

The variable-temperature flowing afterglow/Langmuir probe (VT-FALP) technique is a most successful marriage of the versatile flowing afterglow and the Langmuir probe diagnostic technique (Smith and Adams 1983, 1984b). Recently, it has been used to determine the coefficients for dissociative recombination of several interstellar molecular ions down to a temperature of 95 K (Adams et al. 1984b; Smith and Adams 1984c). This is an important development, since data on this class of ionic reactions is very sparse at low temperatures. Although merged beam data on dissociative recombination are available, they cannot be applied to interstellar conditions with any confidence.

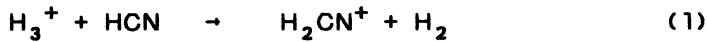
Recent data obtained using the VT-SIFT, IT, CRESU and VT-SIFDT will be presented in Sections 3 and 4. Data obtained using the VT-FALP will be presented in Section 5.

3. BINARY ION-NEUTRAL REACTIONS

Although a very large amount of data are available on ion/neutral reaction rate coefficients, k , and product branching ratios, it is still insufficient to satisfy the increasing demands of the more sophisticated chemical models of ISC. A good deal of the data is contained in compilations which are non-critical and thus they are often misused. Fortunately, new data obtained with the techniques discussed above, together with recent new theory describing collisional rate coefficients, k_c , are removing much of the uncertainty in the k values adopted for interstellar models.

As stated above experimental data have been available for many years which indicate that when $k \approx k_c$, then the k are sensibly independent of temperature. However until recently such measurements could only be obtained down to 80 K (using the VT-SIFT) and then only for non-condensable (non-polar) molecules. Recently, Rowe et al (1985) have used the CRESU technique to show that the reactions of He^+ and N^+ with several non-polar molecules, which had previously been shown to proceed at or near the collision rate at 300 K and 80 K, also proceed at the collisional rate (i.e. $k = k_c$) at 8 K. This is in accordance with classical ion-induced dipole (Langevin) collision theory (Gioumousis and Stevenson 1958). To account for the influence on k_c of the presence of a permanent dipole in the reactant molecule, Su and Bowers (1973) introduced their average dipole orientation (ADO) theory. At room temperature, an increase in k_c by as much as a factor of three above the Langevin value is predicted for reactants with large dipole moments, a prediction well substantiated by experiment. However, little reliable data on ionic reactions involving polar molecules are available at low temperatures for obvious practical reasons

(i.e. condensation problems). Thus, the room temperature values for k_C predicted by the ADO theory (k_{ADO}) have routinely been used in interstellar models. Recently, however, Clary (1985) has given further theoretical consideration to the collisional rate coefficients for ion-polar molecule collisions and concluded that k_C for appreciably exothermic reactions will increase dramatically with reducing temperature, exceeding the k_{ADO} at 300 K by more than an order-of-magnitude at ISC temperatures for very polar molecules. This clearly has serious implications for interstellar modelling. A recent experimental check has been carried out using the VT-SIFT down to 200 K by determining the k for some exothermic proton transfer reactions e.g.



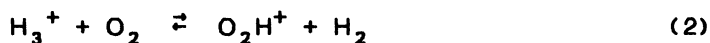
Exothermic proton transfer reactions are a good test of collision theory predictions since they invariably occur at the collisional rate (Adams and Smith 1983). The k for reaction (1), i.e. $k(1)$, was measured to be some 50 percent larger than k_{ADO} at 300 K and precisely in accordance with the theoretical prediction of Clary (Clary et al 1985). Using the CRESU technique, Marquette et al (1986) have determined the k for the reactions of C^+ and N^+ ions with the polar molecules H_2O and NH_3 at 27 K and they observed, as expected, a large increase in k above the 300 K value. Clary's theory indicates the k_C to be rotational (j) state specific, i.e. the k_C increases with decreasing j quantum number, being greatest for molecules in $j = 0$. This is often the state of interstellar polar molecules. Adams et al. (1985b) have considered the implications of these developments to interstellar chemistry and indicated approximate values to be used for the k_C in terms of temperatures and the permanent dipole moments of the reactant molecules. It is clear that the reactions of ions with polar molecules at the low temperatures of ISC are proceeding much faster than hitherto assumed in ion-chemical models and so this chemistry needs to be re-evaluated.

A solution to a long-standing problem in interstellar chemistry followed from these advances in our understanding. For some years, the observed relative number densities of HCS^+ to CS in dense ISC could not be reconciled with the expected production and loss rates for these species, i.e. the observed HCS^+/CS ratio was some 10-100 times greater than model predictions. This anomaly has been removed since, following Clary's work. It is now recognised that the reactions of the very polar molecule CS are much faster than had been assumed previously. This enhances the production rate of HCS^+ (from CS) and the destruction rate of CS. Additionally, a VT-SIFT study of the reactions of HCS^+ demonstrated that the proton affinity of CS is much greater than previous estimates had indicated (Smith and Adams 1985b) meaning that HCS^+ ions are relatively unreactive in ISC. It has also been shown that the dissociative recombination rate of HCS^+ with electrons is relatively small, which further diminishes the loss rate of the HCS^+ in ISC. This solution to the HCS^+/CS problem has been reported by Miller et al. (1985), who also suggested that other protonated polar molecules may hence be present in relatively high concentrations in ISC. It is exciting to note that protonated HCN (HCNH^+) has recently been detected in Sgr.B2 (Ziurys and Turner 1986) in concentrations consistent with the rapid production rate predicted using the new collision theory.

A note of caution is necessary however, regarding the adoption of

collisional rate coefficients at ISC temperatures for reactions that have never been studied in the laboratory. Clary (1985) clearly states that in order to adopt his approach for the determination of k_c , the reaction must be appreciably exothermic. In practice, the exothermicity need only be one to two tenths of an electron volt, to which the large majority of reactions included in interstellar models conform, but nevertheless it is a point which must be considered.

Sometimes, the uncertainties in thermochemical data (e.g. proton affinities, bond energies, etc.) make it impossible to determine if a particular reaction is exothermic or endothermic. When it is appreciated that a reaction need only be ≈ 0.01 eV endothermic to prevent it from occurring under the low temperature conditions of ISC, then great care needs to be taken in predicting the k for such reactions in ISC. For example, it might be thought that the reaction:



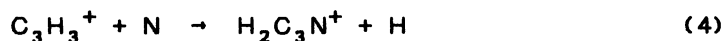
would proceed in ISC producing the O_2H^+ ion, the detection of which could be a way to determine the O_2 density. This would be a reasonable deduction based on the measured k for this reaction at 300 K ($k(2) = 6.7 \times 10^{-10} \text{cm}^3 \text{s}^{-1}$). However, a VT-SIFT study (Adams and Smith 1984a) of both the forward and reverse rate coefficients for reaction (2) clearly shows that the $\text{H}_3^+ + \text{O}_2$ reaction is endothermic by 0.014 eV, an amount which is sufficient to ensure that O_2H^+ cannot be produced by this reaction in cold ISC.

Similar VT-SIFT studies have been carried out on the reactions:



The forward and reverse rate coefficients have been determined at 200, 300 and 520 K which clearly show that HCl can be efficiently produced in ISC by the forward (proton transfer) reaction. The exothermicity of the reaction is 0.12 eV which renders the rate of the reverse reaction negligible in ISC. These data together with a discussion of the production and loss of HCl in ISC are given in a recent paper (Smith and Adams 1985c).

The amount of reliable ion/neutral reaction rate data is now large and continues to grow, largely because of the exploitation of SIFT apparatuses. Much valuable data arises from measurement programmes designed to elucidate specific problems in interstellar chemistry which have been revealed by clever modelling exercises. One such problem, for which a solution is gradually emerging, is the origin of the cyanopolyne molecules. Much effort has been given to this both by experimentalists and theorists. The models reveal (Herbst et al. 1984) that the reaction:



is potentially important and recent experiments (Lindinger priv. comm.) indicate that $k(4)$ is $\approx 10^{-10} \text{cm}^3 \text{s}^{-1}$ at 300 K. If this $k(4)$ were as large at ISC temperatures, then reaction (4) followed by dissociation recombination of the product $\text{H}_2\text{C}_3\text{N}^+$ ions could produce HC_3N in the abundance observed in ISC (dissociative recombination is discussed further

in Section 5). A detailed SIFT study of the reactions of HC_3N has been carried out (Knight et al. 1986) and the results briefly discussed in the context of ISC chemistry. Destruction mechanisms for HC_3N are identified and routes to higher order cyanopolynes are tentatively proposed, such as the condensation reaction:



Dissociative recombination of the product ion can then produce HC_5N .

Much effort has been directed to the sequence of H-atom abstraction reactions which converts N^+ ions to NH_4^+ in ISC. Initially, attention was directed to the final step in the sequence:



Both VT-SIFT and IT experiments have revealed the unusual nature of this reaction: $k(6)$ decreases with decreasing temperature reaching a minimum at ≈ 100 K and then rapidly increases as the temperature decreases further (Adams and Smith 1984b). Recently, attention has been directed towards the first reaction in the sequence:



The IT experiments had indicated that the rate of this reaction reduced dramatically with reducing temperature implying that it is endothermic. Now CRESU experiments (Marquette et al. 1985) have confirmed this and VT-SIFDT studies (Adams and Smith 1985a) of the reactions of N^+ with H_2 , HD and D_2 have provided accurate endothermicities for these reactions. The endothermicity of reaction (7) is found to be (11 ± 3) meV. The implication of these data to ISC chemistry have been discussed by Adams et al. (1984a).

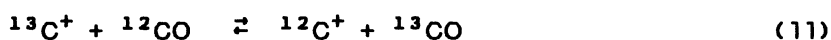
There is a growing interest in the chemistry and physics of the shocked regions of interstellar gas. In hydrodynamic shocks, reactions between neutral radical species apparently play a major role in the chemistry (Dalgarno 1985). In MHD shocks, ions can be accelerated to high velocities and this can drive endothermic ion/neutral reactions (Draine 1985). Thus, the reaction:



which is endothermic by 0.4 eV becomes important (Adams et al. 1984a). SIFDT studies of the rate coefficient for this reaction have been carried out as a function of the centre-of-mass energy, E_{cm} , of the reactants. At the "threshold energy", i.e. $E_{\text{cm}} = 0.4$ eV, which is not untypical of expected energies in MHD shocked regions of the ISC (Draine and Katz 1986), $k(8) \approx 5 \times 10^{-11} \text{cm}^3 \text{s}^{-1}$ which is large enough to make reaction (8) an important source of CH^+ in such regions. This reaction, and other aspects of the reactions of kinetically excited ions are discussed by Adams et al. (1984a). A detailed SIFDT study has recently been carried out of the reactions of S^+ , SH^+ and SH_2^+ with H_2 . These endothermic reactions may be important in the synthesis of sulphur-bearing molecules in shocked regions. A

detailed paper on these data will appear in due course (Adams et al. 1986).

A particular class of binary ion/neutral reactions which result in the fractionation of heavy isotopes into interstellar molecules are the near-thermoneutral isotope exchange reactions. These are exemplified by the reactions:



Detailed VT-SIFT studies of many such reactions have been carried out in which k_f the forward (exothermic) and k_r the reverse (endothermic) rate coefficients have been measured down to 80 K. Thus enthalpy and entropy changes (ΔH and ΔS) have been determined in most cases. Also the kinetics of these reactions are quite predictable in that, in all cases studied, the k_f increase towards their respective k_c at low temperatures and indeed a useful rule for isotope exchange is that at ISC temperatures, $k_f = k_c$. From the known values of ΔH (or estimated values where measured values are not available) combined with values of k_c , the k_r can be deduced. For reaction (9), the very large $|\Delta H|/R = 462$ K means that $k_r(9)$ is negligible at ISC temperatures. This reaction is the primary route to HD production in ISC. The efficient production of H_2D^+ via reaction (10) is a first stage in the production of deuterated interstellar molecules. H_2D^+ readily transfers a deuteron (or a proton) to many interstellar molecules, and the large $|\Delta H|/R \approx 230$ K for the reaction at ISC temperatures ensures that $k_r(10)$ is negligible and the $\text{H}_2\text{D}^+/\text{H}_3^+$ abundance ratio is appreciable. (Note, that $|\Delta H|/R$ is very temperature dependent for reaction (10), Smith and Adams 1984a). Thus, fractionation of deuterium occurs into interstellar molecules, which explains the enhanced D/H ratios observed in many species. Reaction (11) is largely responsible for the large $^{13}\text{C}/^{12}\text{C}$ ratio in interstellar CO relative to the ratio in the solar system (Smith and Adams 1980). A detailed review of isotope exchange has been given by Smith and Adams (1984a) and the interstellar implications are discussed in other papers (e.g. Smith et al. 1982). We have also recently studied the isotope exchange reactions:



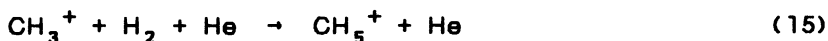
The k_f and k_r were measured at 300 K and 120 K (Adams and Smith 1985b). As expected, the k_f for both reactions increase with decreasing temperature; at 120 K they are about 15 to 20% of the k_c for the reactions, and thus we expect them to be close to k_c at ISC temperatures. The very large ΔH for both reactions also implies very small k_r values and thus D-atoms are fractionated into the HCO^+ and N_2H^+ ions via these reactions. H-atom reactions have also been studied by Federer et al. (1985). The importance of reaction (12) to ISC chemistry has been discussed by Dalgarno and Lepp (1984).

4 RADIATIVE ASSOCIATION AND COLLISIONAL ASSOCIATION

Radiative association reactions are now commonly included in ion-chemical models of interstellar molecular synthesis and much has been written on the subject. The process is exemplified by the reaction:

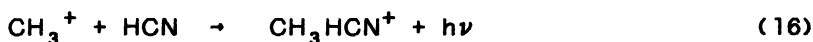


In which the excited intermediate complex $(\text{CH}_5^+)^*$ is prevented from dissociating back to the reactants by the emission of radiation, $h\nu$. These processes are relatively inefficient at room temperature and so are difficult to study directly. However, the analogous three-body (collisional) association can readily be studied.



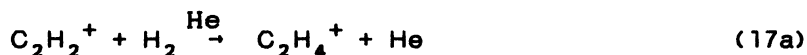
In practice, a three-body (or ternary) association rate coefficient, k_3 , is obtained from which a lifetime against unimolecular decomposition, τ_d , for the intermediate complex $(\text{CH}_5^+)^*$ is derived by a standard method (e.g. see the review by Bates 1986). Theory predicts (and experiments show) that τ_d varies with temperature, T , as $\tau_d \propto T^{-\ell/2}$ where ℓ is the number of rotational degrees of freedom in the separated reactants. Thus for reaction (15), τ_d varies as $T^{-5/2}$. The k_3 versus T have been determined for many ternary association reactions (Meot-ner 1979; Adams and Smith 1983) including many reactions of CH_3^+ with interstellar non-polar and polar molecules (Smith and Adams 1978a; Adams and Smith 1981). Hence τ_d values can be obtained appropriate to the low temperatures of ISC. Combination of these τ_d with estimated radiative lifetimes for the excited intermediate complexes, τ_R , provides values for the radiative association rate coefficients k_R for the analogous binary reactions. When this procedure is applied to reaction (15), k_R is estimated to be $\approx 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at 13 K (assuming $\tau_R = 10^{-3} \text{ s}$). In a unique IT experiment, $k_R(14)$ has been measured directly to be $1.1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ at 13 K (Barlow et al. 1984). The agreement between these results gives credence to the indirect method for estimating k_R values from ternary rate data and not least to the choice at 10^{-3} s for τ_R .

Ternary association rate coefficients are greatly enhanced when the bond strength of the reactant ion/reactant molecule is large. Such is the case for the reactions of CH_3^+ with polar molecules e.g. H_2O , HCN . Then the τ_d and hence the k_R will be very large for these reactions at ISC temperatures. For example, the reaction:

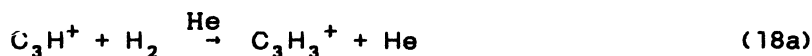


will be very significant. These reactions are therefore very important in the synthesis of interstellar molecules: reaction (16) (followed by dissociative recombination) could be the major route to interstellar CH_3CN . Such reactions take on greater importance than previously thought now it is appreciated that the initial capture rate (i.e. the k_c) is much greater than previously assumed, perhaps approaching $10^{-7} \text{ cm}^3 \text{ s}^{-1}$, following the work of Clary (1985) and Adams et al. (1985) discussed above (Section 3).

Worthy of special note is the observation in a recent VT-SIFT study that ternary association rate coefficients (and by inference radiative association rate coefficients) are greatly increased when parallel, slightly endothermic, binary channels are available in ion/molecule reactions. For example, in the reaction:



channel (17b) is only 70 meV endothermic and is a 15% product in the reaction at 300 K. At 80 K, the association channel (17a) is totally dominant and the reaction rate coefficient is large. This is observed for several such reactions and we have called the phenomenon 'endothermic trapping' (Ferguson et al. 1984). A similar situation occurs in the reaction



In this case, channel (18b) is only a few meV endothermic. The association channel (18a) is very efficient and we propose that the analogous radiative association reaction:

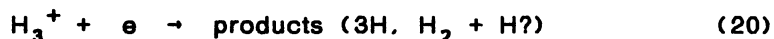


followed by dissociative recombination of the C_3H_3^+ with electrons, is the most probable route to the synthesis of the first 'ring' molecule, C_3H_2 , observed in ISC (Matthews and Irvine 1985). More experiments are needed to substantiate this proposal; these are in progress.

5 DISSOCIATIVE RECOMBINATION

Dissociative recombination of molecular ions with electrons is usually invoked as the neutralization process which generates the neutral molecules observed in ISC. The pioneering studies of dissociative recombination were carried out by Biondi and his co-workers (e.g. Bardsley and Biondi 1970; Biondi 1973). These studies established the order-of-magnitude of the dissociative recombination coefficients, α , at 300 K for most species to be in the range 10^{-7} to $10^{-6} \text{cm}^3 \text{s}^{-1}$ and, in accordance with theoretical predictions, a weak inverse temperature dependence has generally been observed ($\propto T^{-1/2} - T^{-1}$). It is also observed that α tends to be correlated with the complexity of the recombining ion, for example at 300 K, $\alpha(\text{O}_2^+) = 2 \times 10^{-7} \text{cm}^3 \text{s}^{-1}$ and $\alpha(\text{NH}_4^+) = 1.4 \times 10^{-6} \text{cm}^3 \text{s}^{-1}$ (Alge et al. 1983). When α is large ($\alpha > 10^{-6} \text{cm}^3 \text{s}^{-1}$), it is observed to increase only slowly with decreasing temperature. A useful review of some laboratory techniques used to measure α together with lists of α values for many reactions has appeared recently (Mitchell and McGowan 1983). However, since that review, we have exploited our VT-FALP experiment to determine the α for several molecular ions down to 95 K (Smith and Adams

1984c). Included in the study were the reactions:



The values of $\alpha(\text{HCO}^+)$ and also $\alpha(\text{N}_2\text{H}^+)$ and $\alpha(\text{CH}_5^+)$ at 300 K were in acceptable agreement with a previous determination (Adams et al. 1984b). Both $\alpha(\text{HCO}^+)$ and $\alpha(\text{N}_2\text{H}^+)$ varied approximately as T^{-1} between 300 K and 95 K, whereas $\alpha(\text{CH}_5^+)$ which has the large value of $1.5 \times 10^{-6} \text{ cm}^3\text{s}^{-1}$ at 95 K, varies more slowly with temperature as expected. The importance of these studies to interstellar chemistry is that they support the usual assumption that a value of $\alpha \approx 10^{-6} \text{ cm}^3\text{s}^{-1}$ is appropriate for most molecular ions at ISC temperatures. However, a major surprise was that the H_3^+ reaction (20) proceeded immeasurably slowly under the conditions of the VT-FALP experiment within the temperature range 95–600 K. This is quite contrary to previous observations in a pulsed afterglow (Leu et al. 1973) which indicated an $\alpha(\text{H}_3^+) = 2.3 \times 10^{-7} \text{ cm}^3\text{s}^{-1}$ at 300 K. The VT-FALP measurements placed an upper limit of $2 \times 10^{-8} \text{ cm}^3\text{s}^{-1}$ on $\alpha(\text{H}_3^+)$ at all temperatures within the range given above. Recently, this upper limit has been lowered to $10^{-11} \text{ cm}^3\text{s}^{-1}$ (Adams and Smith, unpublished). Similar results were also obtained for $\alpha(\text{D}_3^+)$. This surprising result is in accordance with recent theoretical predictions for ground vibrational state H_3^+ ions (Michels and Hobbs 1984). A finite $\alpha(\text{H}_3^+)$ is predicted for vibrationally excited H_3^+ ions, a prediction which is supported by the VT-FALP experiments. Since H_3^+ in cool ISC is most surely vibrationally relaxed, then dissociative recombination of H_3^+ in dense ISC does not occur at a significant rate. This has major implications to ISC chemistry and physics. For example, compared to previous estimate, H_3^+ will be present in greater abundance in ISC. Also, the Watson model for estimating the electron density, n_e , in ISC (Watson 1976) has to be abandoned since it assumed a large $\alpha(\text{H}_3^+)$. We have addressed this problem and other implications of a negligible $\alpha(\text{H}_3^+)$ in a recent paper (Smith and Adams 1984c). The large n_e implied by the negligible $\alpha(\text{H}_3^+)$ also means a more rapid chemistry and so a more rapid evolution of interstellar molecules.

Clearly, measurements are required of the α for many more interstellar ions at low temperatures. These are underway in our laboratory using the VT-FALP apparatus and there may be further surprises. For example, our recent estimate of $\alpha(\text{HCS}^+)$ showed it to be rather small for a triatomic ion; this contributed to a solution of the HCS^+/CS problem (Millar et al. 1985) which was discussed in Section 3.

An urgent need is for data relating to the neutral products of dissociative recombination reactions. At present, intelligent guesswork is all that can be used in ISC chemistry. This problem is now being seriously considered by experimentalists and progress is very likely in the next year or so.

6 CONCLUDING REMARKS

Recent developments in laboratory techniques are enabling a wide variety of ionic reactions important in ISC to be studied at low temperatures.

These studies have confirmed that the collisional rate coefficients, k_c , for ion/neutral reactions involving non-polar molecules vary little with temperature and are as predicted by simple collision theory. For polar molecules, the situation has been clarified by recent theory and experiments which indicate rapid increases in k_c as temperature decreases towards ISC temperatures. So, values for k_c can now be calculated with confidence at ISC temperatures. It is essential to emphasise again, however, that the k for all ion/neutral reactions are not equal to k_c and careful judgement is required in the choice of k values for use in models of ISC chemistry when experimental values are unavailable. Similar remarks apply to the α for dissociative recombination; a canonical value of $\approx 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ is appropriate for most polyatomic ions at ISC temperatures. More experimental data are, however, required at suitably low temperatures for a wider range of interstellar molecular ions. Also there is a pressing need for experimental data on the products of dissociative recombination reactions.

It is gratifying to note that as more experimental kinetic data have become available, discrepancies between model predictions and observed abundances of molecules in ISC are being reconciled. As the data flow continues, doubtlessly more problems will be solved and a greater understanding of the physics and chemistry of ISC will be obtained.

APPENDIX

ESTIMATION OF THE MAGNITUDES OF COLLISIONAL RATE COEFFICIENTS FOR THE REACTIONS OF IONS WITH POLAR MOLECULES AT INTERSTELLAR TEMPERATURES.

The ACCSA (Adiabatic Capture Centrifugal Sudden Approximation) method of calculating collisional rate coefficients, k_c , for ion/polar molecule reactions due to Clary is a development of previous similar theoretical work. Reference to the previous work and an outline of the ACCSA theory is given by Clary (1985) and by Clary et al. (1985). The interstellar implications of this work are discussed by Adams et al. (1985b). The ACCSA theory indicates that k_c is rotational (j) state specific, i.e. that k_c increases with decreasing rotational excitation of the molecule, k_c being greatest for $j = 0$, a common state for polar interstellar molecules. Here we designate $k_c(j = 0)$ as k_o and we designate the Boltzmann averaged k_c over all rotational states at a given temperature, T , as k_b .

To date, the k_c have been measured for only a few ion/polar molecule reactions at temperatures below 300 K (see Clary et al. 1985; Marquette et al. 1985b); however these measurements give great credence to the ACCSA predictions. A rapid increase in k_c (and therefore in both k_o and k_b) as T is reduced below 300 K is predicted by the theory and this is confirmed by experiment. The increase in k_c is particularly rapid below 50 K and especially for molecules with large permanent dipole moments, μ_D . The calculation of k_j and hence k_b can be carried out for any ion/linear polar molecule reaction at any temperature using the ACCSA theory with the computer programme developed by Clary. Fortunately, however, we find by inspection of the computer calculated values for k_o and k_b for several reactions involving reactant molecules having different μ_D , that k_o and k_b can conveniently be parameterised as:

$$k_o = \frac{1.89 \times 10^{-7}}{\mu^{1/2}} T^{-0.52} (\mu_D - 0.3) \text{ cm}^3 \text{ s}^{-1}$$

$$k_b = \frac{1.63 \times 10^{-7}}{\mu^{1/2}} T^{-0.59} (\mu_D - 0.3) \text{ cm}^3 \text{ s}^{-1}$$

where μ is the reduced mass (in amu) of the reactant ion/molecule pair, μ_D is the dipole moment of the molecule in Debyes and T is the absolute temperature in K. These relationships are good fits to the ACCSA predicted values within the temperature range 5 – 50 K, and for $\mu_D > 1$ Debye which are appropriate to most polar interstellar molecules. For temperatures > 50 K, the above relationships somewhat underestimate the k_c (ACCSA) for molecules with small μ_D and somewhat overestimate k_c (ACCSA) for very polar molecules. Thus, for example, at 200 K the k_b for the $\text{H}_3^+ + \text{HCl}$ ($\mu_D = 1.08$ Debye) reaction predicted by the above relationship is $\approx 20\%$ smaller than k_c (ACCSA) and the k_b for the $\text{H}_3^+ + \text{HCN}$ ($\mu_D = 2.98$ Debye) reaction is greater than k_c (ACCSA) by $\approx 20\%$.

It is apparent that, using the parameterised expressions, the k_o and k_b for many ion/polar molecule reactions can be calculated with sufficient accuracy for the purposes of ion-chemical modelling of interstellar clouds within the temperature range 5–200 K. At 300 K and above, the k_b are the most appropriate rate coefficients to use, and except for very polar molecules, are sufficiently closely approximated by k_{ADO} (see the main text). The following table of examples illustrates the differences between k_o , k_b and k_{ADO} for the reactions of both a light and a heavier ion (H_3^+ and HCO^+) with both HCl (a small $\mu_D = 1.08$ Debye) and HC_3N (a very polar molecule, $\mu_D = 3.6$ Debye) at 10 K and 300 K.

	10 K		300 K	
	k_o	k_b	k_b	k_{ADO}
$\text{H}_3^+ + \text{HC}_3\text{N}$	1.12(-7)	8.21(-8)	1.3(-8)	8.26(-9)
$\text{HCO}^+ + \text{HC}_3\text{N}$	4.38(-8)	3.22(-8)	5.1(-9)	3.24(-9)
$\text{H}_3^+ + \text{HCl}$	2.67(-8)	1.96(-8)	3.6(-9)	3.36(-9)
$\text{HCO}^+ + \text{HCl}$	1.11(-8)	8.13(-9)	1.5(-9)	1.39(-9)

Here, for example, 1.12(-7) is equivalent to $1.12 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$. Note the large differences between the k (10 K) and k (300 K) and the significant differences between the k_o and k_b at 10 K. Note especially the enormous values of k_o and k_b for the $\text{H}_3^+ + \text{HC}_3\text{N}$ reaction, which are an order-of-magnitude greater than k_{ADO} at 300 K and some 10^2 times greater than the often-used canonical k of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$!

Finally, it is important to note that Clary (priv. comm.) has extended his theory to embrace the reactions of ions with non-linear polar molecules and his predicted k_c are in good agreement with the (as yet) limited amount of experimental data available for such reactions. Also he has recently

shown that when the reactant ion is also polar then this can enhance the k_c values beyond the already enormous values indicated by the published ACCSA theory.

REFERENCES

- Adams, N. G. , and Smith, D. 1981, Chem. Phys. Letters, **79**, 563.
- Adams, N. G. , and Smith, D. 1983, in Reactions of Small Transient Species: Kinetics and Energetics, eds. A. Fontijn and M. A. A Clyne (New York: Academic Press), p. 311.
- Adams, N. G. , and Smith, D. 1984a, Chem. Phys. Letters, **105**, 604.
- Adams, N. G. , and Smith, D. 1984b, Int. J. Mass Spectrom. Ion Proc. , **61**, 133.
- Adams, N. G. , and Smith, D. 1985a, Chem. Phys. Letters, **117**, 67.
- Adams, N. G. , and Smith, D. 1985b, Ap. J. (Letters), **294**, L63.
- Adams, N. G. , Smith, D. , and Millar, T. J. 1984a, M. N. R. A. S. , **211**, 857.
- Adams, N. G. , Smith, D. , and Alge, E. 1984b, J. Chem. Phys. , **81**, 1778.
- Adams, N. G. , Smith, D. , and Ferguson, E. E. 1985a, Int. J. Mass Spectrom. Ion. Proc. , **67**, 67.
- Adams, N. G. , Smith, D. , and Clary, D. C. 1985b, Ap. J. (Letters), **296**, L31.
- Adams, N. G. , Smith, D. , Lindinger, W. , Villinger, H. and Millar, T. J. 1986, in preparation.
- Alge, E. , Adams, N. G. , and Smith, D. 1983, J. Phys. B, **16**, 1433.
- Albritton, D. L. 1978, Atom. Data Nucl. Data Tables, **22**, 1.
- Bardsley, J. N. , and Blondi, M. A. 1970, Adv. Atom. Mol. Phys. , **6**, 1.
- Barlow, S. E. , Dunn, G. H. , and Schauer, M. 1984, Phys. Rev. Letters, **52**, 902
- Bates, D. R. 1986, in Fundamental Processes in Atomic Collision Physics, ed. H. Kleinpoppen, (New York: Plenum Press), in press.
- Biondi, M. A. 1973, Comments Atom. Molec. Phys. , **4**, 85.
- Clary, D. C. 1985, Mol. Phys. , **54**, 605.
- Clary, D. C. , Smith, D. , and Adams, N. G. 1985, Chem. Phys. Letters, **119**, 320.
- Dalgarno, A. 1985, in Molecular Astrophysics, ed. G. H. F. Diercksen et al. , (Dordrecht: Reidel), p. 281.
- Dalgarno, A. , and Black, J. H. 1976, Rept. Prog. Phys. , **39**, 573.
- Dalgarno, A. , and Lepp, S. 1984, Ap. J. (Letters), **287**, L47.
- Draine, B. T. , and Katz, N. S. 1986, Ap. J. , submitted.
- Draine, B. T. 1985, in Molecular Astrophysics, ed. G. H. F. Diercksen et al. , (Dordrecht: Reidel), p. 295.
- Federer, W. , Villinger, H. , Tosi, P. , Bassi, D. , Ferguson, E. E. , and Lindinger, W. 1985, in Molecular Astrophysics, ed. G. H. F. Diercksen et al. , (Dordrecht: Reidel), p. 649.
- Ferguson, E. E. , Fehsenfeld, F. C. , and Schmeltekopf, A. L. 1969, Adv. Atom. Mol. Phys. , **5**, 1.
- Ferguson, E. E. , Smith, D. , and Adams, N. G. 1984, J. Chem. Phys. , **81**, 742.
- Gioumousis, G. , and Stevenson, D. P. 1958, J. Chem. Phys. , **29**, 294.
- Graedel, T. E. , Langer, W. D. , and Frerking, M. A. 1982, Ap. J. Suppl. , **48**, 321.
- Hartquist, T. W. , Black, J. H. , and Dalgarno, A. 1978, M. N. R. A. S. , **185**, 643.
- Herbst, E. 1983, Ap. J. Suppl. , **53**, 41.
- Herbst, E. , and Klemperer, W. 1976, in Physics of Electronic and Atomic Collisions, ed. J. S. Risley and R. Geballe, (Seattle: Univ. of Washington Press), p. 62.
- Herbst, E. , Adams, N. G. , and Smith, D. 1983, Ap. J. , **269**, 329.

- Herbst, E., Adams, N. G., and Smith, D. 1984, Ap. J., **285**, 618.
- Huntress, W. T. Jr. 1977, Ap. J. Suppl., **33**, 495.
- Knight, J. S., Freeman, C. G., McEwan, M. J., Smith, S. C., Adams, N. G., and Smith, D. 1986, M. N. R. A. S., in press.
- Leu, M. T., Biondi, M. A., and Johnsen, R. 1973, Phys. Rev., **A8**, 413.
- Leung, C. M., Herbst, E., and Huebner, W. F. 1984, Ap. J. Suppl., **56**, 231.
- Luine, J. A., and Dunn, G. H. 1981, 12th Int. Conf. on Physics of Electronic and Atomic Collisions, Gatlinburg, Tennessee, July 1981, p. 1035.
- Marquette, J. B., Rowe, B. R., Dupeyrat, G., and Roueff, E. 1985a, Astron. Astrophysics, **147**, 115.
- Marquette, J. B., Rowe, B. R., Dupeyrat, G., Poissant, G., and Rebrion, C. 1985b, Chem. Phys. Letters, **122**, 431.
- Matthews, H., and Irvine, W. M. 1985, preprint.
- McIver, R. J. Jr. 1978, Rev. Sci. Instrum., **49**, 111.
- Meot-ner, M. 1979, in Gas Phase Ion Chemistry, Vol. 1, ed. M. T. Bowers, (New York: Academic Press), p. 198.
- Michels, H. H., and Hobbs, R. H. 1984, Ap. J. (Letters), **286**, L27.
- Millar, T. J. 1985, in Molecular Astrophysics, ed. G. H. F. Diercksen et al., (Dordrecht, Reidel), 613.
- Millar, T. J., Adams, N. G., Smith, D., and Clary, D. C. 1985, M. N. R. A. S., **216**, 1025.
- Mitchell, J. B. A., and McGowan, J. W. 1983, in Physics of Ion-Ion and Electron-Ion Collisions, ed. F. Brouillard and J. W. McGowan, (New York: Plenum Press), p. 279.
- Prasad, S. S., and Huntress, W. T. Jr. 1980, Ap. J., **239**, 151.
- Rowe, B. R., Dupeyrat, G., Marquette, J. B., Smith, D., Adams, N. G., and Ferguson, E. E. 1984a, J. Chem. Phys., **80**, 241.
- Rowe, B. R., Dupeyrat, G., Marquette, J. B., and Gaucherel, P. 1984b, J. Chem. Phys., **80**, 4915.
- Rowe, B. R., Marquette, J. B., Dupeyrat, G., and Ferguson, E. E. 1985, Chem. Phys. Letters, **113**, 403.
- Smith, D., and Adams, N. G. 1977, Ap. J., **217**, 741.
- Smith, D., and Adams, N. G. 1978a, Ap. J. (Letters), **220**, L87.
- Smith, D., and Adams, N. G. 1978b, in Kinetics of Ion-Molecule Reactions, ed. P. Ausloos, (New York: Plenum Press), p. 345.
- Smith, D., and Adams, N. G. 1979, in Gas Phase Ion Chemistry, Vol. 1, ed. M. T. Bowers, (New York: Academic Press) p. 1.
- Smith, D., and Adams, N. G. 1980, Ap. J., **242**, 424.
- Smith, D., and Adams, N. G. 1981, Int. Rev. Phys. Chem., **1**, 271.
- Smith, D., and Adams, N. G. 1983, in Physics of Ion-Ion and Electron-Ion Interactions, ed. F. Brouillard and W. M. McGowan (New York: Plenum Press), p. 501.
- Smith, D., and Adams, N. G. 1984a, in Ionic Processes in the Gas Phase, ed. M. A. Almoester-Ferreira (Dordrecht: Reidel), p. 41.
- Smith, D., and Adams, N. G. 1984b, in Swarms of Ions and Electrons in the Gas Phase, ed. W. Lindinger, T. D. Mark and F. Howorka, (Vienna: Springer-Verlag), p. 284.
- Smith, D., and Adams, N. G. 1984c, Ap. J. (Letters), **284**, L13.
- Smith, D., and Adams, N. G. 1985a, in Molecular Astrophysics, ed. G. H. F. Diercksen et al., (Dordrecht: Reidel), p. 453.
- Smith, D., and Adams, N. G. 1985b, J. Phys. Chem., **89**, 3964.

- Smith, D., and Adams, N. G., 1985c, Ap. J., **298**, in press.
 Smith, D., Adams, N. G., and Alge, E. 1982, Ap. J., **263**, 123.
 Smith, D., Adams, N. G., and Alge, E. 1984, Chem. Phys. Letters, **105**, 317.
 Su, T., and Bowers, M. T. 1973, Int. J. Mass Spectrom Ion Phys., **12**, 347.
 Su, T., and Bowers, M. T. 1979, in Gas Phase Ion Chemistry, Vol. 1, ed. M. T. Bowers, (New York: Academic Press), p. 83.
 Walls, F. L., and Dunn, G. H. 1974, J. Geophys. Res., **79**, 1911.
 Watson, W. D. 1976, Rev. Mod. Phys., **48**, 513.
 Ziurys, L., and Turner, B. E. 1986, Ap. J. (Letters), in press.

DISCUSSION

P.K. GHOSH: Are the internal states thermalised in the low temperature ion-molecule reaction experiments?

D. SMITH: The rotational states of the reactant ions and molecules are certainly thermalised on the buffer gas in SIFT and CRESU experiments (except, for example, the ortho/para states of H₂ at low buffer gas temperatures). The vibrational states are more problematical and so experimental checks have to be made for any residual vibrational excitation, particularly in the reactant ions. One can usually ensure that the ions are not significantly vibrationally excited by adjusting the gas pressure in the ion sources from which the reactant ions are obtained.

P.K. GHOSH: Besides CH₃⁺, why the other hydrocarbon ions have not been considered for the formation of CH₅⁺?

D. SMITH: We cannot identify any other significant process for CH₅⁺ production. Although CH₄⁺ reacts slowly with H₂ to produce CH₅⁺, the CH₄⁺ must presumably be produced from CH₄ which is itself produced from CH₅⁺.

TAKAYANAGI: It is remarkable that a simple idea such as the adiabatic approach can theoretically predict ion-polar molecule reaction rates which are in very good agreement with experiments. I am very happy to see this success since the Clary's theory is essentially the same as ours which was published five years ago (Sakimoto and Takayanagi, J. Phys. Soc. Japan **48**, 2076 (1980), Sakimoto, Chem. Phys. **63**, 419 (1981), **85**, 273 (1984), Chem. Phys. Letts. **116**, 86 (1985)).

D. SMITH: The importance of the previous work prior to that of Clary is properly noted in Clary's papers on this subject.

JACKSON: (i) Are dissociative collisional association reactions such as CH₃⁺ + H₂ → CH₄⁺ + H important? (ii) What is your new value for the dipole moment⁴ of CS?

D. SMITH: (i) The production of CH₄⁺ from the reaction of CH₃⁺ with H₂ is very endothermic and so it cannot occur in cold interstellar

clouds. It could occur in high velocity MHD-shocked regions. (ii) The dipole moment of CS is 1.98 Debye.

DALGARNO: Can you tell us what is the position with regard to low temperature behaviour of neutral-neutral reaction?

D. SMITH: For neutral radical-radical reaction, the theory was originally developed by Clary; at low temperatures, he predicted a rapid rise in reaction rate with temperature. It is difficult to understand why this happens.

TURNER: It is certainly of interest to us that your new rates for the reaction $H_3^+ + HCN \rightarrow HCNH^+$ are large, and suggest an explanation for the surprisingly large fractional abundance that we (Ziurys and Turner 1986) have recently found in our detection of $HCNH^+$ in the ISM (see also Ziurys and Turner, this volume). Since so many ion-molecule reaction rates are indeed coming out so large, might not we need to consider whether destruction processes for $HCNH^+$ are also larger than expected? I should mention that our present observational results for $HCNH^+$ abundance is correlated with that of HNC and not that of HCN.

HERBST: There is a significant difference in ion-polar rate coefficients between linear and non-linear neutral reactants because non-linear species have metastable rotational states and less "dipole locking".

D. SMITH: An interesting comment. Clary is now extending his theory to embrace non-linear polyatomic molecules.

GOEL: Could the observed isotopic variations in meteorites in the $^{16}O/^{17}O$ ratio be explained on ion-molecular exchange reactions rather than the nucleogenetic effects?

SMITH: At present we do not know enough about the $^{16}O-^{17}O$ isotope exchange rates to give a clear answer.

GLASSGOLD: (i) What ionization fraction enters into the analysis of the HCS^+/CS ratio? (ii) Isn't your limit to the H_3^+ recombination rate close to radiative recombination rate?

D. SMITH: (i) This is discussed in our recent paper (Millar et al. 1985). (ii) Our upper limit to the $H_3^+ + e$ recombination coefficient is $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and is indeed close to the radiative recombination rate coefficient.

ROUEFF: We are presently studying the sulphur chemistry related to interstellar shock conditions. One crucial point in our calculations is the endothermicity of the $SH^+ + H_2 \rightarrow H_2S^+ + H$ reaction, which is found to be quite different from spectroscopic and thermochemical data. Have you any comments on this?

D. SMITH: According to the available thermochemical data, the reaction is endothermic by 0.55 eV. We have obtained some support for this value from our laboratory studies of this reaction.