

What Do We Know and What Do We Need to Know?

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Abstract. I review recent progress in determining the rate coefficients appropriate to modelling interstellar chemistry, give some information on appropriate databases from which rate coefficients can be obtained, and point to the importance of the gas-grain interaction in determining molecular abundances. Although many of the fundamental gas-phase reactions have been studied in the laboratory, the failure of the models to explain the observations of water and methanol in cold clouds indicates that grains may have an important role, both in acting as a surface for freeze-out and in the synthesis of complex molecules. The major challenge in astrochemistry is to develop a more quantitative model for the role of grains and, in some cases, to incorporate a better, probably more complex, physical model for interstellar clouds.

Keywords. astrochemistry — molecular data — ISM: molecules

1. Introduction

The synthesis of molecules in space is driven at low temperatures by ionisation – from ultraviolet photons in regions of low extinction, the so-called ‘diffuse clouds’ – and from cosmic ray particles in regions of high extinction, the so-called ‘dense’ or ‘dark clouds’. In the latter objects, cosmic ray ionisation of molecular hydrogen produces the H_2^+ ion which reacts ‘instantaneously’ with H_2 to produce the ion H_3^+ . As the proton affinity (PA) of H_2 is very low – only N, O_2 , F, and the noble gases have lower PAs – this ion undergoes proton transfer reactions with almost all interstellar species, in particular with atoms, initiating chains of reactions, most importantly with H_2 , which produce many of the molecules we detect in these clouds. Cosmic rays also ionise helium to produce He^+ which has an ionisation potential (IP) of some 24 eV. Thus collisions of He^+ with neutral molecules are very destructive and tend to break bonds and fragment the molecules. Thus, He^+ plays a destructive role in interstellar chemistry; at the same time the radicals and ions it produces are themselves able to take part in synthetic reactions which produce more complex species. The reaction between He^+ and H_2 is exothermic but, fortunately for astrochemistry, does not occur. If it did occur at the collisional rate, H_2 would be destroyed much faster than it is and few molecules would be formed.

The presence of ionisation in cold clouds leads to a number of classes of reaction which are important in molecular clouds. Ion-neutral reactions generally proceed via a complex which is lower in energy than the reactants so that such reactions tend to occur at the collisional rate if exothermic. For neutrals with no or only a small permanent electric dipole moment, the rate coefficient is given by the well known Langevin expression

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which is independent of temperature. This leads to the happy situation that theory or experiments at room temperature provide rate coefficients which can be used at low (10 K) temperatures. For neutrals which have a significant dipole moment a correction to the Langevin formula is required. Several forms are possible but the Average-Dipole-Orientation (ADO) method provides a reasonably accurate value for the rate coefficient, many of which behave as $T^{-0.5}$ below 300 K. The invention of the Selected Ion Flow Tube (SIFT) in the early 1980s by David Smith and Nigel Adams revolutionised the laboratory study of ion-neutral reactions so that today well over 1000 reactions relevant to astrochemistry have been measured in the laboratory, with a significant number of these measured at temperatures down to 80 K and lower (Anicich 2004).

Neutral-neutral reactions can also occur at low temperatures. In general such reactions proceed through an intermediate complex which has energy larger than that of the reactants so that, even if exothermic, they tend to possess activation energy barriers. The weaker interaction between neutrals also tends to give rate coefficients with a $T^{0.5}$ behaviour. In recent years, however, there has been a great advance in the laboratory study of neutral reactions at low temperatures, particularly with the CRESU technique, as described by Sims in this volume. It has long been known that radical-radical reactions often proceed without activation barriers; the recent experiments show that they often possess rate coefficients with a T^{-n} dependence, and that radical-molecule reactions can also be fast at low temperature.

The ionisation caused by UV photons and cosmic ray particles produces electrons as well as positively charged molecular ions. Collisions between these species have large rate coefficients and are usually destructive in nature, with several product channels. In general one usually assumes that the major channel involves the loss of a H atom to produce an observed species, in line with the expectation that the channel involving the least rearrangement of orbitals might be preferred. Until recently only a few such reactions have been studied at the low energies appropriate to interstellar clouds but the use of storage rings as a means for producing low energy interactions between cooled species and to measure the product distribution has thrown up several surprises (see Geppert this volume).

One final class of reaction important in interstellar clouds is that of radiative association in which two species, most commonly an ion and a neutral, stabilise in collision through the emission of a photon. Such reactions are difficult to study in the laboratory where higher densities than in interstellar clouds means that the association complex is stabilised by collisions rather than radiation. Thus, most of the information we have on radiative association rate coefficients depends on three-body measurements coupled with a theoretical calculation to provide the appropriate radiative rate coefficient.

In order to identify the important reactions in a molecular cloud we consider the time-scales in which a molecular ion M^+ is destroyed by reaction with H_2 , electrons and other neutral species, X. Using typical reaction rate coefficients these time-scales are $10^9/n(H_2)$, $10^6/n(e)$, and $10^9/n(X)$, respectively. Since $n(e) \sim 10^{-4}n$ and $n(X) \sim 10^{-6}n$ in diffuse clouds, loss of M^+ is dominated by reaction with H_2 as long as the fractional abundance of H_2 is greater than about 0.1. Dissociative recombination is only important if the rate coefficient of the H_2 reaction is less than $10^{-10} \text{ cm}^3 \text{ s}^{-1}$. To a first approximation, the chemistry of diffuse clouds is 'simple'; one needs to consider only reactions of molecular ions with H_2 and electrons. The inclusion of radiative recombination with atomic ions and photodissociation of neutral molecules 'completes' the chemistry. In dense clouds, the fractional ionisation is less by a factor of 10^3 – 10^4 , so that dissociative recombination and reactions with X are important only if the ion does not react or reacts very slowly with

H₂. Again, to a first approximation, the chemistry of dense clouds is ‘simple’. Finally, we note that since $n(\text{H}_2) \sim 10\text{--}10^6 \text{ cm}^{-3}$ in interstellar clouds, ions can be assumed to react ‘instantaneously’ with H₂ when they are able to do so.

In the following, I will briefly describe the important processes in diffuse and dense interstellar clouds and indicate areas in which we have good fundamental data. As we shall see there are several instances in which, despite having good gas-phase data, the observations are not understood and perhaps point to the importance of the gas-grain interaction and, in some cases, to the naive physical models adopted.

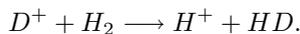
2. Diffuse Clouds

Diffuse interstellar clouds are characterised by having a low extinction which enables both visible and, more importantly, UV photons to penetrate them completely. The photons also provide a significant source of heating, through photoelectric emission and photoionisation, so that diffuse cloud temperatures are typically in the range 50–100 K. The gas phase association of H atoms is a very slow process so that the H₂ molecule is formed on interstellar dust particles and subsequently ejected vibrationally and rotationally excited by its formation energy into the gas-phase. Although the photodissociation of H₂ is a line process – so that the molecule self-shields effectively – the resulting fraction of H₂ is often small, so that the cloud is predominantly atomic in nature. In these objects the flux of UV photons is such that cosmic ray ionisation is always much less important than photoionisation of atoms such as C, S, Si and Mg and it is this process which enables the ionisation fraction to be large, $\sim 10^{-4}$. Nevertheless, cosmic ray ionisation of atomic hydrogen is important since it cannot be ionised, in common with O and N, by the interstellar UV field.

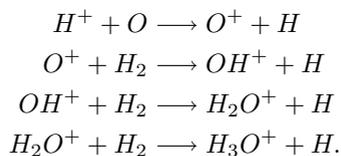
Although the formation of the simplest interstellar molecule, H₂, is on grain surfaces, the relatively large abundance of the HD, together with the fact that its photodissociation rate is 100–1000 times faster than that of H₂, since it does not self-shield efficiently, indicates that this species must be formed 100–1000 times faster than H₂, that is in the gas phase rather than on grains. The initiating reaction in the formation of HD is the charge exchange:



followed by



Observations of HD in diffuse clouds allow one to estimate the rate at which H atoms are ionised by cosmic rays and lead to values in the range $5\text{--}50 \times 10^{-17}$ ionisations per H atom per second. The ionisation rate can also be estimated from observations of OH in warm diffuse clouds. In this case the chemistry is initiated by a charge transfer reaction which is slightly endothermic, by an energy equivalent to 240 K:



The H₃O⁺ produced by this fast chain of reactions then undergoes dissociative recombination with electrons to produce O, OH and H₂O, with the water being photodissociated rapidly to form OH. By comparing the loss rate of H⁺ with O atoms to that of

loss via radiative recombination with electrons, one concludes that in clouds with temperatures greater than about 50 K, every H^+ ion produced leads to the formation of an OH radical. Assuming that the chemistry is in steady state, a good assumption in diffuse clouds, one derives the abundance of OH as:

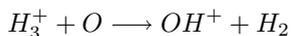
$$n(\text{OH}) = \frac{\zeta n(\text{H})}{\beta},$$

where ζ is the cosmic ray ionisation rate of H atoms and β is the photodissociation rate of OH, which has been calculated quantum mechanically. Since all of the above reactions involving H_2 have been measured in the laboratory, as has the dissociative recombination of H_3O^+ , observation of OH and H leads to an estimate for ζ which agrees with the values derived from observations of HD.

In general, the conclusion is that the observations of diffuse clouds are well described by gas-phase chemistry. Surface chemistry is important only for H_2 and possibly for NH (Wagenblast *et al.* 1993) although, to date, no models have yet incorporated the latest experimental results on the dissociative recombination of N_2H^+ which produces NH twice as efficiently as N_2 (Geppert *et al.* 2004); previous models had assumed that NH was not formed by this means.

3. Dense Clouds

In dense clouds, the cosmic ray ionisation of H_2 drives the chemistry through proton transfer reactions involving H_3^+ with atoms such as C, O, and S. Again, taking the O-H chemistry as an example, the initiating reaction is:



followed by reactions with H_2 and the dissociative recombination of H_3O^+ with electrons as described in § 2. In dense clouds, there are no externally-produced photons, except in surface layers, and destruction of H_2O occurs through reactions with abundant ions such as He^+ , C^+ , H_3^+ , and HCO^+ . All of these reactions have been studied experimentally; all are fast, proceeding at the collisional rate. OH is also destroyed by these same ions, although in this case no experimental information is available. Nonetheless, we believe that theoretical estimates of the appropriate rate coefficients are probably accurate to within 30%. A more important loss for the radical OH is through fast reactions with other neutral atoms and radicals, in particular with the abundant atoms O, N, C, S, and Si. These reactions, which produce oxides, are thought to be fast. Indeed this is found experimentally for the reaction of OH with O, measured at temperatures down to 160 K, with N, measured down to 100 K, and S, measured at 300 K. The reaction between O and OH is thought to be the main production route to O_2 which itself, as a radical, is destroyed most efficiently in reaction with C atoms to form CO, measured to be fast down to 15 K, and also by ion reactions, the most important of which have all been measured. One concludes from this that the abundances of O, OH, and H_2O should be calculated, even from such a simple chemical model, to a fair degree of accuracy. In fact, the opposite is the case; dense clouds are severely under-abundant, particularly in O_2 and H_2O , compared to model predictions (see Liseau, this volume). This might be because the gas-grain interaction affects abundances through the process of freeze-out or that a more complex description of the physical model is required.

4. New Experimental Rate Coefficients

Recent experimental advances are covered elsewhere in this volume by Sims, Geppert & McCall; here I highlight a few results and their influence on chemical models.

4.1. Dissociative Recombination

The use of storage rings to study dissociative recombination (DR) has led to several new, and sometimes very surprising, results, particularly in regard to product channels. In a very beautiful experiment, McCall *et al.* (2004) combined a supersonic expansion jet source with the CRYRING to measure the DR rate coefficient, α , of rotationally cold H_3^+ down to very low energies and found $\alpha = 6.7 \times 10^{-8} (T/300)^{-0.52} \text{ cm}^3 \text{ s}^{-1}$. This experiment finally ends the debate on the magnitude of this rate coefficient, a debate which has raged for over 20 years. DR is an inefficient loss of H_3^+ in dense clouds, where proton transfer reactions with abundant neutrals such as CO dominate, but is important in the diffuse gas, including those lines of sight in which the infrared absorption lines of H_3^+ have been detected and leads to even higher cosmic ray ionisation rates than derived from the OH and HD observations mentioned in § 2 (see McCall, this volume).

The CRYRING has been extensively used by Geppert and collaborators to study the DR of many important astrophysical ions including HCO^+ , N_2H^+ , HOCO^+ , HC_3NH^+ , and CH_3OH_2^+ , among others. Some of the results have been surprising. Although HCO^+ recombines to form CO, only one-third of the recombinations of N_2H^+ form N_2 . This new route to NH formation in dense clouds increases its calculated abundance by a factor of three. More importantly, DR now provides a mechanism by which N_2 and N_2H^+ can be depleted in high-density regions, even if N_2 has a low binding energy on interstellar grains since the NH formed in DR can freeze-out more effectively on grains than N_2 . One observational consequence is that ND should possess the same deuteration fractionation as N_2D^+ and should be detectable close to 492 GHz. In many cases, product channels consisting of three or more neutrals are produced; for CH_3OH_2^+ only 5% of the product is methanol, compared to the usual assumptions in model calculations that methanol is produced in either 50% or 100% of recombinations. Figure 1 shows the influence of the small branching ratio on the calculated methanol abundance in a dense cloud model. The methanol abundance is almost directly related to the reduced branching ratio, in fact the reduction is slightly greater than the factor of 10 in the branching ratios due to less efficient recycling of protonated methanol. This figure shows that the observed methanol abundance in dense clouds, typically 10^{-9} – 10^{-8} , is difficult to reproduce. We return to this point in § 4.3.

4.2. Neutral-Neutral Reactions

A significant number of neutral-neutral reactions have been measured at low temperature, particularly in the CRESU experiment. Among the important astrophysical species measured have been reactions of CH, CN, and C_2H . Smith, Herbst & Chang (2004) have analysed the low-temperature behaviour of some 300 neutral-neutral reactions included in astrochemical models while the NIST Chemical Kinetics Database (URL: www.kinetics.nist.gov/index.php) contains rate coefficients, based on both theory and experiment, of close to 12,000 neutral reactions, although the data is only complete until the end of 2000. More recent results from the CRESU include reactions of C_2 and C_4H (Sims, this volume). Although total rate coefficients are measured, it is much more difficult to get information on product channels.

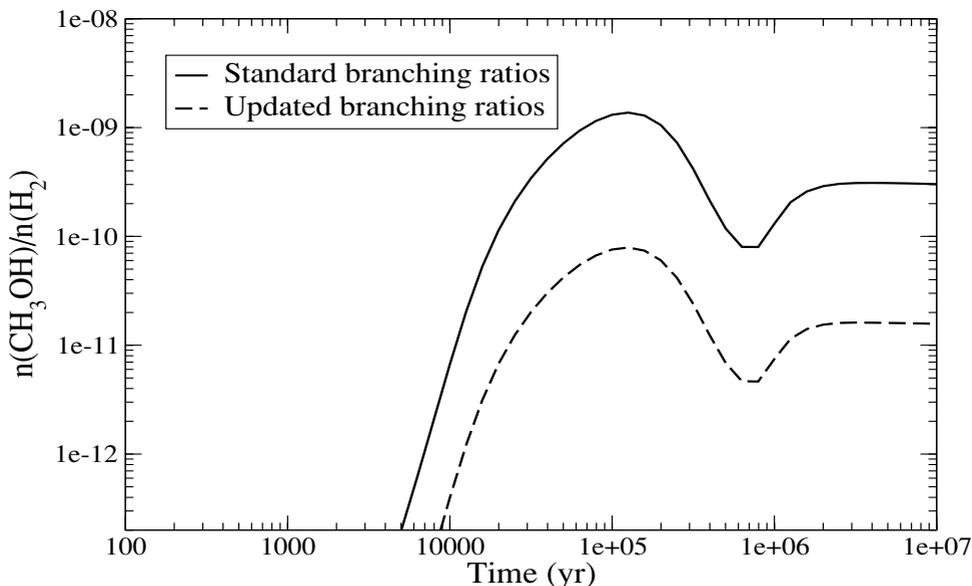


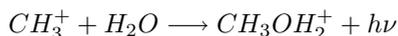
Figure 1. Time-dependent abundance of methanol using a standard branching ratio of 50% and the laboratory-determined value of 5% (Geppert *et al.* 2005).

4.3. Radiative Association

Radiative association reactions such as:



and



are important in building complex species from simpler species. As mentioned in §1, there are very few relevant experimental studies at pressures appropriate to interstellar conditions and rate coefficients are usually evaluated through a combination of theory and experiment. Important new results have been presented for the two systems above. Luca *et al.* (2002) studied the $CH_3^+ + H_2O$ system and derived a rate coefficient of $2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, independent of temperature at low temperatures, compared to the standard value of $5.5 \times 10^{-12} (T/300)^{-1.7} \text{ cm}^3 \text{ s}^{-1}$, based on a theoretical interpretation of a three-body association (Herbst 1985). Such theoretical analysis relies on appropriate experimental information. Recently Bacchus-Montabonel, Talbi & Persico (2000) have used the laboratory data of Gerlich and collaborators to reduce the usually adopted value of the rate coefficient of the $CH_3^+ + H_2$ radiative association from $1.3 \times 10^{-14} (T/300)^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Smith 1989) to $2.4 \times 10^{-15} (T/300)^{-0.55} e^{-30/T} \text{ cm}^3 \text{ s}^{-1}$, a difference of over 1000 at 10 K. Inclusion of this rate coefficient shows that the calculated fractional abundance of methanol never rises above 10^{-10} and in steady-state is only a few times 10^{-12} , failing to reproduce the observed abundance in dense clouds by a factor of 1000. This failure of gas-phase chemistry perhaps indicates a role for the grain surface formation of methanol in such sources. The critical issue then is how solid-state methanol is returned to the gas phase at 10 K.

4.4. Photodissociation

Photodissociation processes are particularly important in diffuse clouds and also in photo dominated regions (PDRs) and in the external envelopes of late-type stars. Here, the data situation is mixed. For small species there is extensive information on cross-sections available from theory or experiment, although in many cases there is no cross-comparison able to be made. Many stable molecules have measured UV absorption but the situation for radicals is poor. There are several excellent articles describing the estimation of photorates for interstellar and cometary molecules (van Dishoeck 1988; Roberge *et al.* 1991; Huebner *et al.* 1992) and web sites are available, through the efforts of J. Crovisier and W. Huebner (URLs: <http://www.usr.obspm.fr/~crovisier/basemole/> and <http://amop.space.swri.edu/>, respectively). However, when one looks in detail the situation is not always clear. As an example consider the unshielded photodissociation rate of methanol. Van Dishoeck (1988) quotes one set of products, H₂CO and H₂, with a rate coefficient of $1.4 \times 10^{-9} \text{ s}^{-1}$. Roberge *et al.* (1991), on the other hand, have two photoionisation channels and one neutral channel, to CH₃ and H₂O, with a rate of $1.2 \times 10^{-9} \text{ s}^{-1}$. Huebner *et al.* (1992) gives 5 channels, 4 of which are applicable to photons in the interstellar medium. The dominant channel in this compilation is H₂CO and H₂, with the rate coefficient for the CH₃ plus H₂O channel being some 12 times smaller. In fact, it turns out that Huebner *et al.* (1992) assumed that 5% of the product channel below threshold gives CH₃ and H₂O. Furthermore, although Roberge *et al.* (1991) quote an experiment to justify the dominance of their preferred channel, the experiment was such that it only monitored the OH production rate and, in fact, suggested that the yield to this channel was low (Nee, Suto & Lee 1985); seemingly, this was mis-interpreted by Roberge *et al.* (1991).

5. Databases

There are a number of databases which deal with fundamental data required for astrochemical modelling. In addition to the sites mentioned in § 4.2 and § 4.4, V. Anicich has provided a compilation of 'all' ion-neutral reactions (JPL Publication 03-19) measured in the period 1936-2003, containing references to some 2300 articles. The data are not evaluated but all individual measurements are listed. Some values for specific rate coefficients are labelled as 'Evaluated' but the values are, in fact, simple averages of all measurements.

With the exception of the NIST Chemical Kinetics Database, all other databases generally reflect the work of one particular individual. As a result they are at the mercy of changing scientific interests but, more usually, of retirement. Thus the Anicich and Huebner databases will no longer be updated, while the NIST database has not been updated since 2000 and Crovisier's since 2002. The lack of appropriate funding support for these databases is certainly an issue of concern.

Two groups have made available specific reaction sets appropriate to interstellar chemistry to the community. Both contain around 4000 reactions among about 400 species. E. Herbst's group at Ohio State University have 3 models available which differ slightly in details (URL: <http://www.physics.ohio-state.edu/~eric/index.html>). T.J. Millar's group at UMIST make similar reaction sets available: RATE99 (URL: <http://www.rate99.co.uk>) and RATE05 (URL: <http://www.udfa.net>). There are some differences in philosophy between the OSU and UMIST databases. The OSU database adopts ion-dipole enhanced rate coefficients where appropriate, and many unmeasured C atom reactions to produce hydrocarbon chains, balancing these with unmeasured

O atom reactions which destroy hydrocarbons. The UMIST database relies more heavily on measured rate coefficients – over one-third of all reactions in RATE05 have been measured. In addition the UMIST databases include high-temperature neutral-neutral reactions so that shock chemistry can be modelled.

RATE04 has been improved over its predecessors in a number of ways. An error in the implementation of cosmic-ray photon-induced reactions was noted by S. Doty. Both the UMIST and OSU implementations incorporate probabilities which are a factor of two too large. This is because the ionisation rate is proportional to $n(\text{H}_2)$ while the extinction due to grains, implicit in the determination of the probability, is proportional to the total density, that is, $2n(\text{H}_2)$. A critical study of the rate coefficients of neutral-neutral reactions at low temperature (Smith, Herbst & Chang 2004) was included, although not all their individual rate coefficients were included, in some cases the NIST data were preferred. New dissociative recombination rates and branching ratios were included, as discussed in § 4.1, and photorates were up-dated using results from the Huebner database and improved literature searches. In addition to the basic ratefile, the UMIST database also contains tables of heats of formation, electric dipole moments, a set of deuterium fractionation reactions, and codes for the calculation of interstellar cloud chemical models.

6. Dust Grains

The discussion on the failure of gas-phase astrochemical models to reproduce the observed methanol abundance in § 4.1 and 4.3 indicated one possible solution – the formation of methanol in the ice mantles from the hydrogenation of CO (see Watanabe, this volume). One of the key parameters in surface chemistry is binding energy, which determines not only mobility on the surface but also residence time, desorption, and thus any resulting gas-phase chemistry. In this regard the recent work by Collings *et al.* (2004) which shows that a molecule can have a number of binding energies depending on its binding site, has important chemical consequences, which have been discussed by Viti *et al.* (2004) and Nomura & Millar (2004). In particular, the spatial distribution of molecules in hot molecular cores shows much more small-scale structure than models in which molecules thermally evaporate at one particular temperature. The determination of accurate binding energies is a critical aspect of surface chemistry since time-scales depend exponentially on them. Although there have been recent efforts at studying surface hydrogenation, there is little quantitative information available on the possibility that radical-radical reactions are effective in cold ices. However, the detections of the highly unsaturated formic acid, HCOOH, in interstellar ices and methyl formate, HCOOCH₃, in comets, indicate that radical reactions might be important. If so, we are a long way from any quantitative modelling of surface chemistry.

7. Conclusions

The rate coefficients of most ion-neutral reactions are well-determined from 25 years of experimental study which have also measured products, and associated theoretical calculations. In particular, reactions of almost all interstellar ions with H₂ have been measured. Of the 2900 or so ion-neutral reactions in the RATE05 database, over 1100 have been measured. However, some important classes of reaction are poorly studied, particularly those involving atoms such as C, N, and O, and several important thermo-neutral reactions need to be investigated at very low temperatures. Although there are many critical radiative association reactions in interstellar chemistry, there are very few

measurements of the two-body processes at the low temperatures of interstellar clouds, and those systems which have been measured have rate coefficients orders of magnitude less than those inferred from three-body association experiments, indicating that previous theoretical estimates of radiative association may be greatly in error.

There has been a great deal of new experimental data on low-temperature neutral-neutral reactions although products are rarely determined. Progress in this field is difficult, both theoretically since interaction energies are small, and experimentally since each system needs a specific detection system to monitor the disappearance of one of the reactants or the identification of products. Smith, Herbst & Chang (2004) have made substantial progress in suggesting rate coefficients at low temperature and have identified several key reactions, mostly involving OH, for further study.

The use of storage rings to determine the rate coefficients and branching ratios of dissociative recombination reactions has produced many surprises, some of which have important implications for the efficiency of molecule formation through ion-molecule chemistry. The importance of the gas-grain interaction has been fully recognised and will present a major challenge to a quantitative understanding of molecular synthesis in cold interstellar clouds over the next 5–10 years.

Acknowledgements

This research has been supported by a grant from PPARC.

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Discussion

GUÉLIN: The reaction rates measured in the laboratory show that some interstellar molecules (*e.g.*, methanol) cannot form in the gas phase and *must* result from grain surface reactions. Can we say equally that some molecules (*e.g.*, HD) *cannot* be formed on grains and *must* result from gas-phase reactions and, if yes, what fractions of the known astrophysical molecules is concerned?

MILLAR: First, I note that the laboratory measurement for the $\text{CH}_3^+ + \text{H}_2\text{O}$ radiative association reaction has not been published in a refereed journal some three years after publication in a conference proceeding, so the status of this one reaction is still uncertain. Certainly the abundance of HD in *diffuse* clouds indicates that it must form in the gas phase. I would also argue that all observed molecular ions – all of which can be formed by proton transfer reactions of H_3^+ with common neutral molecules – are the result of gas phase reactions. This gives a lower limit of 10% or so. I also believe that the vast majority of the molecules observed in TMC-1 are produced in the gas phase, although in some sources, some of these same molecules can be formed most efficiently on grains.

TORNOW: Charnley has proposed a number of proton-transfer reactions relevant for hot cores. Do you have included them into your new data-base RATE 05?

MILLAR: We have been careful to use the Anicich database on ion-neutral reactions to include all proton-transfer reactions appropriate to our species set. However, our database has been set up specifically for diffuse and dense interstellar clouds. We do not include species such as methyl ethyl ether; methyl formate, ethanol and dimethyl ether are included.

VAN DISHOECK: Does the new UMIST database give explicitly the rate coefficients of $\text{C}(J) + \text{X}$, $\text{O}(J) + \text{X}$ etc., *i.e.* as a function of the atomic fine structure level?

MILLAR: No, the database does not give such rate coefficients. Few, if any, such reactions have been studied experimentally.

KROES: CH_3OH is now assumed to form through grains surface reactions in dense clouds. It is experienced as problematic that it is then released from the grains. Why is that so? Could not the energy released in the formation be used to desorb the CH_3OH ?

MILLAR: That, of course, is a possibility although it depends on how exactly the excess energy is partitioned. If the process works in dense clouds, it presumably also happens to the CH_3OH molecules formed in ‘pre-hot-core’ ices. One major issue to understand is why the CH_3OH abundance in hot cores – which is also due to the hydrogenation of CO in an ice – is at least 100 times larger than that in dense clouds.

HERBST: Comment: We have just included desorption via the exothermicity of chemical reaction in our gas-grain code using simple statistical theory.