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D. Smith^a; N. G. Adams^a

^a Department of Space Research, University of Birmingham, Birmingham, England

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MOLECULAR SYNTHESIS IN INTERSTELLAR CLOUDS: RECENT LABORATORY STUDIES OF IONIC REACTIONS

D. SMITH AND N. G. ADAMS

Department of Space Research, University of Birmingham, Birmingham B15 2TT, England

ABSTRACT

The existence of complex molecules in the harsh environment of interstellar diffuse and dense clouds presents the challenging problem as to their mode of synthesis. Currently, this is believed to be predominantly via many parallel and sequential gas phase ion–neutral reactions which build-up large molecular ions which are then neutralized to give the observed molecules. The objective of this paper is to review the current ideas of the most important ion-chemical routes to the observed molecules and to discuss the most recent laboratory data which have supplemented and extended earlier ideas. To this end, the physical conditions within the various types of interstellar clouds and their chemical compositions are first described. The basic ion-chemical models and some of the more important ionic reactions involved in them are then described as they variously apply to both dense and diffuse clouds. Reference is then made to the data obtained recently for the rate coefficients and product ion distributions for a large number of relevant exoergic binary ion–molecule and ion–atom reactions. Attention is then directed towards the process of ion–molecule radiative association which for some time was thought to occur only between C^+ ions and H atoms and H_2 molecules, but which is now thought to occur in many more ion–molecule interactions, including many involving minority neutral species. The very interesting process of isotope exchange in near-thermonutral ion–molecule reactions is then considered since it has been invoked to explain the apparent fractionation of rare isotopes into some of the interstellar molecules. Finally, the various neutralization processes which are required to convert product ions into neutral molecules are discussed briefly, and the paper is ended with some concluding remarks.

1. INTRODUCTION

Ninety per cent of the mass of our galaxy (the Milky Way) resides in the stars. The remaining ten per cent is scattered unevenly throughout interstellar space and is known as the interstellar medium. This interstellar medium is very diverse in nature consisting of several different phases ranging from a ubiquitous very hot tenuous phase (temperature, T , $\sim 10^5$ – 10^6 K, gas density, n , $\sim 10^{-2}$ – 10^{-3} cm^{-3}) and a hot, less tenuous phase ($T \sim 10^4$ K, $n \sim 10^{-1}$ cm^{-3}) to much cooler, denser clouds of gas and dust. In these cooler clouds, T falls to maybe as low as 10 K and n is perhaps as high as 10^6 cm^{-3} . It is in these cool denser clouds that molecules have been detected, molecules which are thought to be produced by a complex gas phase and surface phase chemistry. It was realized as long ago as the late 1930s (Dunham, 1937, 1940; Swings and Rosenfeld, 1937; McKellar, 1940, 1941; Adams, 1941; Douglas and Herzberg, 1941, 1942) that interstellar chemistry was occurring in these clouds when the characteristic absorption lines of CH, CH^+ and CN

were identified in the background visible radiation from several nearby bright stars. Recently, more sophisticated ultraviolet absorption experiments conducted from orbiting satellites have detected and determined the relative concentrations of several diatomic molecules in the so-called 'diffuse' interstellar clouds (Spitzer *et al.*, 1973; Spitzer and Jenkins, 1975; Morton, 1975; Morton and Hu, 1975; Crutcher and Watson, 1976; Snow, 1976, 1977; Black, 1980). However, radio and millimetre wave observations have dominated the emerging picture of interstellar chemistry and, with these techniques, more than 40 different molecules have been detected via their characteristic emissions in these regions of the electromagnetic spectrum. The development of the observational techniques and the order of discovery of the molecules are discussed in several excellent reviews (Rank, Townes and Welch, 1971; Zuckerman and Palmer, 1974; Turner, 1974a; Townes, 1976; Somerville, 1977; Winnewisser, Churchwell and Walmsley, 1979).

To date, more than 50 molecular species have been detected including five positive ion species. Many of these molecules are also seen containing the rarer stable isotopes of their composite elements (*see for example the recent review by Wannier, 1980*). The important question to be addressed in this review is 'how are the molecules synthesized in these hostile regions of space?' or equivalently 'what are the essential processes involved in interstellar chemistry?'. Since most of the complex molecules have been detected in massive aggregates of gas and dust, such as the clouds in the galactic centre and in the Orion nebula, the mechanism of molecule formation on the surfaces of dust grains (with subsequent desorption) was strongly favoured during the earlier years of the subject (McNally, 1972; Turner, 1974b; Cook, 1975; Watson, 1976). More recent opinion favours and evidence is growing in support of gas phase ion chemistry as the dominant mechanism and this is the subject of this review paper. However, grain surface catalysis may still play an important rôle; in fact it is believed to be the mechanism via which H_2 , the most abundant molecular species is synthesized (for further discussion *see Section 3*). The relative importance of the various mechanisms will depend on the physical conditions in the regions in which the molecules are found, that is the gas and dust number densities, the temperature, the radiation field, ionization density, etc. These physical conditions in the various types of clouds are briefly discussed in Section 2.

Within the present knowledge of the mechanisms of formation of interstellar molecules one thing seems certain, binary (2-body) gas-phase ion-neutral reactions play an important rôle. Neutral-neutral reactions involving radical species also probably contribute but reactions between non-radical neutral species play a lesser rôle since the activation energy they usually require is not available at the low ambient temperatures. Also ternary (3-body) reactions cannot be significant at the low ambient gas densities. These principles are recognized in the ion-chemical models of interstellar clouds. We discuss the pioneering work in gas-phase ion-chemical modelling in Section 3. Theories of dust grain catalysis are not included, so we refer the reader to several authoritative papers on this topic (Williams, 1968; Watson and Salpeter, 1972a,b; Pickles and Williams, 1977; Duley, Millar and Williams, 1980; Greenberg *et al.*, 1980; *see also the review by Watson, 1976*).

The earliest ion-chemical models of molecule formation in interstellar clouds were constructed without much laboratory data on the ionic reactions thought to be involved. Also the data which were available had been acquired at room temperature or above and in many cases a step of faith was required to extrapolate them to interstellar cloud conditions. Nevertheless, recent laboratory work has indicated that extrapolations of this kind are valid in many cases but in some critical cases they are unacceptable. The growing interest in this subject has been stimulated by the increasingly sophisticated radio- and millimetre-wave observations which are resulting in the discovery of more interstellar molecules. The parallel development of ion-chemical models has highlighted the need for

laboratory data on ionic reactions at appropriately low temperatures. During the last few years, laboratory experiments have been developed which are providing data at temperatures comparable to those in diffuse interstellar clouds but which, alas, generally are still not able to operate at temperatures as low as those in the coldest clouds. Nevertheless these new experiments are providing data which give new and exciting insights into ion chemistry at very low temperatures and which are suggesting new lines of approach to interstellar chemistry. It is therefore appropriate that this new laboratory work should be reviewed at this stage since, hopefully, it will provide further stimulus to an already active field. Thus in Section 4 we discuss briefly the new advances in laboratory experimentation and consider in a qualitative manner the relevance of the latest laboratory data to interstellar ion chemistry.

In Section 5 we briefly summarize the current status of the subject, mentioning some of the successes and outstanding problems in ion-chemical modelling of interstellar clouds and referring to some requirements and desirable developments in laboratory studies.

2. PHYSICAL PROPERTIES AND COMPOSITION OF INTERSTELLAR CLOUDS

To appreciate the chemistry occurring in interstellar clouds, it is important to be aware of the physical conditions within, and the composition of, the various cloud types. As mentioned above, the interstellar medium is very non-uniform, consisting of clouds of several types separated by a very tenuous inter-cloud phase. The cold clouds in which molecules have been detected vary from the tenuous 'diffuse clouds' to the 'dense clouds', the latter often being subdivided into 'molecular (or black) clouds' and 'dark clouds'. However, it should be said that individual clouds as a whole cannot be expected to fall neatly into one of these fairly narrowly-defined categories. Much of the following description of cloud types is taken from the authoritative reviews by Dalgarno (1975), Dalgarno and Black (1976), Herbst and Klemperer (1976a,b), Watson (1976, 1977), and Huntress (1977).

The diffuse clouds, as the name suggests, have small visual extinctions as a result of their tenuous nature ($\sim 10^2$ atoms and molecules per cc). It is in these clouds that molecules were first detected via their characteristic absorption lines in the background starlight. Since destructive short wavelength radiation also penetrates these clouds, then the molecules observed in them are only of the simple (largely diatomic and triatomic), strongly bonded types. Larger molecules, if formed, will have short lifetimes against photodestruction (Sandell and Mattila, 1975; Sandell, 1978). All types of interstellar clouds consist largely of atomic and molecular hydrogen in varying proportions. In diffuse clouds H and H₂ are present in comparable proportions, other elements are expected to exist largely in their atomic forms (mostly C, N, O) at concentrations roughly in accordance with their cosmic abundances (see Table 1). Ionization is created in the outer regions of these clouds by ultraviolet radiation with wavelengths greater than that

TABLE 1. Cosmic abundances, by number relative to hydrogen, of some of the elements (*from* Allen, 1973).

H	He	Ne	O	C	N	Fe	Mg	Si	S
1	9(-2)	8(-4)	7(-4)	3(-4)	9(-5)	4(-5)	3(-5)	3(-5)	2(-5)
Na	Al	Ca	Ni	F	P	Cl	Cr	Mn	
2(-6)	2(-6)	2(-6)	9(-7)	3(-7)	3(-7)	3(-7)	2(-7)	1(-7)	

corresponding to the photoionization threshold for atomic hydrogen, shorter wavelength radiation than this being strongly absorbed in the outermost reaches of the clouds. In the inner regions where the ultraviolet radiation field is less intense, cosmic rays contribute significantly to the ionization. Because of the relatively large cosmic abundance of carbon and because the ionization energy of atomic carbon is smaller than that of atomic hydrogen, C^+ is expected to be an important primary ion in diffuse clouds and so much of the ion chemistry is assumed to start with C^+ (this is discussed in Section 3). The intense radiation field also ensures that the temperatures within these clouds are relatively high ($\lesssim 100$ K). A representative, extensively studied diffuse cloud is that in the direction of the star Zeta Ophiuchi (ζ Oph) and since we will refer to this cloud from time-to-time in this review, it is worthwhile to give here as an example some of the physical and chemical parameters of this cloud. Thus the total gas density n is $\sim 10^2$ – 10^3 cm^{-3} , the electron density is ~ 0.2 cm^{-3} , the temperature is ~ 50 K and the H atom and H_2 concentrations are comparable and many orders of magnitude greater than those of the other molecules (i.e. HD, CO, CH, CN and OH). These data come mainly from Morton (1975).

The dense interstellar clouds are much more varied in their properties than the diffuse clouds. They consist largely of accumulations of molecular hydrogen and 'dust' grains and this combination ensures that they are opaque to visible and short wavelength radiation. They are however, relatively transparent to radio and millimetre waves which thus allows the molecules in these clouds to be detected via their characteristic emissions in these regions of the electromagnetic spectrum. Because ultraviolet starlight is prevented from penetrating to great depths, then large, complex molecules can survive and indeed are observed in these dense clouds. As mentioned previously, dense clouds are usually subdivided into 'molecular' clouds and 'dark' clouds.

The molecular clouds are the most massive objects in the galaxy (as much as 10^5 times the mass of the sun) and are very active regions in which star formation is occurring continuously. Indeed always associated with them are early-type stars ('O' and 'B' types), H II regions (the hot, luminous gaseous envelopes surrounding new stars), and strong infrared emissions emanating from newly forming stars (protostars). Large density and temperature variations exist within these clouds which are undergoing local gravitational collapse ('clumping'), but typically the gas densities lie within the range 10^3 to 10^6 cm^{-3} and the temperatures range from about 30 K to 100 K. The mass motions and turbulence in these clouds can generate shock fronts in which the local temperature can be high and this can initiate chemical reactions which would otherwise be endothermic. These shocks, which have been invoked to enhance the formation rate of CH^+ via the endoergic $C^+ + H_2$ reaction (Elitzur and Watson, 1978), could obviously dramatically modify the chemistry of these shocked regions. They are also thought to initiate local gravitational collapse and consequently the production of protostars. The most complex polyatomic molecules yet detected in interstellar clouds (e.g. $(CH_3)_2O$, CH_3CH_2CN) are in these molecular clouds and because of the varied physical conditions within them the detailed chemistry producing these molecules must be very complex.

The dark clouds are smaller quiescent regions in which there is much less activity than in the molecular clouds. The gas densities are, on average, smaller (10^2 to 10^4 cm^{-3}) and because of their quiescent nature they are colder with temperatures in the range 10–20 K. Indeed, recent direct spectroscopic evidence (Zuckerman and Kuiper, 1980) and indirect evidence from ion-chemical modelling (*see* page 297) indicates that the temperatures in these clouds may be below 10 K. They contain simpler molecular species (e.g. H_2CO , HCN, HCO^+) than the molecular clouds and this provides important clues to the chemical processes which are occurring within them. The physical and chemical properties of nine dark clouds have recently been discussed by Snell (1981). The properties of the diffuse, molecular and dark clouds have been discussed in detail by Myers (1978).

The elemental composition of interstellar clouds is of great importance not only from the viewpoint of their chemistry but also from an astrophysical and cosmological viewpoint. The compositions of the various gas clouds relative to each other (in terms of their distance from the galactic centre) and relative to the solar system composition are related to such profound questions as 'how fast has nuclear processing of primordial hydrogen and deuterium in the interior of stars proceeded during the lifetime of the universe?' (see e.g. Audouze and Tinsley, 1974) and 'is the universe open or closed?' (Gott *et al.*, 1974). Nuclear processing undoubtedly occurs on the interior of stars (see *CNO Isotope in Astrophysics*, edited by J. Audouze, 1977) and the new elements formed are carried into the interstellar medium via the stellar winds which 'blow' out from the surfaces of certain types of stars. Thus the composition of interstellar clouds is expected to vary depending on their proximity or otherwise to such active stars. The component elements of most clouds can only be observed when combined into molecules (except for a few diffuse clouds relatively near to the solar system which can be studied via atomic absorption) and chemical processes occurring within the clouds can influence the elemental composition of the observed molecules according to the reactivity of the element. These processes must therefore be considered in deriving the elemental composition of the material of a cloud as a whole from observations of molecular abundances. These principles are equally important when deriving isotopic abundances of a given element (e.g. D/H, $^{13}\text{C}/^{12}\text{C}$) from molecular observations, since zero-point energy differences in the molecules can lead to isotope fractionation (see pages 295–298). In the absence of observational data on the elemental composition of the gas clouds, the cosmic abundances of the elements are often used as a guide. This, however, can be a dangerous procedure not only because of the nucleosynthesis arguments above, but because some elements may be preferentially condensed onto the surfaces of dust grain (Duley and Millar, 1978). Indeed the dust grains are probably composed of a few selected cosmically abundant elements and their oxides (e.g. Na, Mg, Si.). It is perhaps due to this condensation that many of these cosmically abundant elements are absent from the molecular emission spectra of interstellar clouds, including surprisingly chlorine.

A source of ionization is required also in the dense clouds. Since they are opaque to radiation at ultraviolet and X-ray wavelengths, then galactic cosmic rays are invoked as the primary ionization source. Ionization densities in dense clouds are difficult to determine and one has to rely on estimates obtained from ion-chemical models. We discuss these models in the light of the recent laboratory data on ion-molecule reactions in Section 4. For the moment, estimates of the upper limit ionization density, n_e , relative to that of H_2 vary between 10^{-8} and 10^{-7} (Guélin *et al.*, 1977; Watson, Snyder and Hollis, 1978b; Turner and Zuckerman, 1978; Langer *et al.*, 1978; Wootten, Snell and Glassgold, 1979; Snell and Wootten, 1979). These densities, although very small, are considered adequate to initiate the ion-neutral reactions which are thought to build the larger molecular ions from which the observed neutral molecules are produced via electron positive-ion dissociative recombination or other neutralization processes (see pages 299–301).

In concluding this section, it must be re-emphasized that the whole of an individual cloud cannot be expected to fall into one of the rather narrow categories discussed above. For example, the much-studied Orion Nebula is seen to consist of differing phases ranging from a hot H II region to a molecular cloud (for further discussion see the review by Winnewisser *et al.*, 1979), and the diffuse ζ Oph cloud referred to above is thought to consist of a relatively cool, dense inner region and a warmer, less dense outer region (Black and Dalgarno, 1977). Also the different parts of molecular clouds are in differing phases of gravitational collapse and so they will exist as gas clouds for varying lengths of time. Credible ion-chemical schemes must therefore take into account these finite lifetimes, but it is well known (Langer and Glassgold, 1976) that the characteristic times for most

ion-chemical reactions are within the estimated lifetimes of most clouds. Scoville and Hersh (1979) and Kwan (1979) have recently discussed the lifetimes of giant molecular clouds which apparently can be as long as 10^8 years; that is of the order of one per cent of the lifetime of our galaxy and the present universe.

Thus the interstellar clouds are very varied, complex and harsh environments in which it is somewhat surprising to find complex molecules. But molecules do exist in them and thus the chemistry which results in their formation must be explained. This is the major objective of the remainder of this review.

3. MOLECULES OBSERVED AND ION-CHEMICAL MODELS FOR THEIR FORMATION

In this section, we first present a list of the molecules observed in interstellar clouds and briefly comment on their nature. Secondly we outline the ion-chemical models which have been proposed and developed to describe the formation of some of the observed molecules. These models range from the earliest qualitative models which appeared in the literature only as recently as 1972 (Solomon and Klemperer, 1972; Herbst and Klemperer, 1973) to the more recent detailed quantitative models of specific diffuse clouds (Black and Dalgarno, 1977; Black, Hartquist and Dalgarno, 1978; Federman and Glassgold, 1980) and the time-varying models which describe the chemical evolution in the dense clouds (Langer and Glassgold, 1976; Iglesias, 1977; Prasad and Huntress, 1980a,b; Suzuki, 1980; Huntress, Prasad and Mitchell, 1980). We shall only discuss the qualitative and semi-quantitative models; detailed description of the other more sophisticated models is inappropriate here so these will only be mentioned and the appropriate references given.

Molecules observed

To date more than 50 different molecular species have been detected in the various types of interstellar clouds and in many cases they are also seen containing the rare stable isotopes of the elements (e.g. ^{13}CO) in addition to the corresponding common isotope (i.e. ^{12}CO). Especially rich sources of molecules are the Orion cloud complex and the giant molecular clouds near to the galactic centre. The current list of molecules is given in Table 2 where the molecules which contain rare isotopes are also identified. The existence and observation of these rare isotopes offer vital opportunities to study galactic evolution (*see* page 294). The molecular species vary from the simple diatomic species to large polyatomics, the largest being HC_9N the most recently detected member of the cyanopolyacetylene series (Brotten *et al.*, 1978) the others being HC_3N , HC_5N , HC_7N . These are just a few of the many organic molecules observed, several of which are unsaturated. This is a strong indicator of gas phase production rather than dust grain catalysis. Another interesting feature of the list of molecules is the presence of several oxygen and sulphur analogues, for example CO/CS , NO/NS , SiO/SiS , $\text{H}_2\text{O/H}_2\text{S}$, $\text{H}_2\text{CO/H}_2\text{CS}$, etc. Note that only five positive ions have been detected to date, these being CH^+ , HCO^+ , N_2H^+ , CO^+ and HCS^+ , the last two being very recent discoveries. Also note the absence from the list of the stable species N_2 , O_2 and CO_2 . It is almost certain that these species are relatively abundant in interstellar clouds but because of their symmetry they are not readily observable by millimetre wave techniques. Many other species, including a variety of positive ions, are surely present and remain to be detected. Certainly many molecular lines have been observed which are, as yet, unidentified.

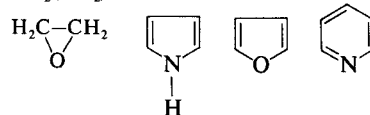
Before a particular species can be detected and positively identified its spectrum must be known in the appropriate wavelength region. This is usually obtained by laboratory

TABLE 2. The observed interstellar molecules listed in order of their atomicities, including those molecules seen containing rare isotopes. The five positive ion species are underlined. Also included are several molecules which have been searched for but not as yet detected (*from Thaddeus, 1979*).

H ₂ , HD	CH ₄
CH	CH ₂ NH
<u>CH⁺</u>	CH ₂ CO
<u>OH</u>	NH ₂ CN
C ₂	HCOOH
CN	C ₄ H
CO, ¹³ CO, C ¹⁷ O, C ¹⁸ O, ¹³ C ¹⁸ O	HC ₃ N, H ¹³ CC ₂ N, HC ¹³ CCN, HC ¹³ CN
<u>CO⁺</u>	-----
NO	CH ₃ OH, CH ₃ OD, ¹³ CH ₃ OH
CS, ¹³ CS, C ³³ S, C ³⁴ S	CH ₃ CN
SiO, ²⁹ SiO, ³⁰ SiO	NH ₂ CHO
NS	-----
SO, ³⁴ SO	CH ₃ NH ₂
SiS	CH ₃ C ₂ H
-----	CH ₃ CHO
H ₂ O, HDO, H ₂ ¹⁸ O	CH ₂ CHCN
C ₂ H	HC ₃ N, DC ₃ N
HCN, DCN, H ¹³ CN, HC ¹⁵ N	-----
HNC, DNC, HN ¹³ C	HCOOCH ₃
HCO	CH ₃ C ₃ N
<u>HCO⁺</u> , DCO ⁺ , H ¹³ CO ⁺ , HC ¹⁸ O ⁺	-----
<u>N₂H⁺</u>	(CH ₃) ₂ O
HNO	C ₂ H ₂ OH
H ₂ S	C ₂ H ₂ CN
<u>HCS⁺</u>	HC ₇ N
OCS, O ¹³ CS	-----
SO ₂	HC ₉ N

NH ₃ , NH ₂ D, ¹⁵ NH ₃	
C ₂ H ₂	
H ₂ CO, HDCO, H ₂ ¹³ CO, H ₂ C ¹⁸ O	
HNCO	
H ₂ CS	
C ₃ N	

Species searched for but not detected
H₂D⁺, CH₃F, N₂O, HCO₂⁺, PN, NO₂,
O₃, CH₃Cl, C₃H₇CN, C₆H, C₅N, HC₁₁N,
CH₂(NH₂)COOH



spectroscopic observations (e.g. Alexander, Kroto and Walton 1976; Kirby, Kroto and Walton, 1980; Quade and Suenram, 1980) sometimes aided by theoretical calculations (e.g. Klemperer, 1970; Wahlgren *et al.*, 1973; Herbst and Klemperer, 1974, Kraemer and Diercksen, 1976; Green, 1980). Also the species must be present in sufficiently large concentrations and have an adequate state-to-state transition probability in an appropriate wavelength region. In practice, more than one line in the characteristic spectrum has to be detected before a definite identification is announced, especially for millimetre wave spectra, since many complications exist in identifying characteristic lines. Not least amongst these complications are the Doppler shifts on the lines due to the high relative velocities between the detector and the gas clouds. Such severe complications inevitably lead to differing interpretations of the spectra and controversy regarding some of the identifications. Currently, doubt is being cast onto the CH₄ identification of Fox and Jennings (1978) and the NH₂D identification of Turner *et al.* (1978) and Rodriguez Kuiper, Zuckerman and Kuiper (1978). It has been pointed out that an alternative identification of the CH₄ lines and all but one of the NH₂D lines is methyl formate,

HCOOCH₃ (Eldér *et al.*, 1980), so these identifications of CH₄ and NH₂D must now be considered to be tentative.

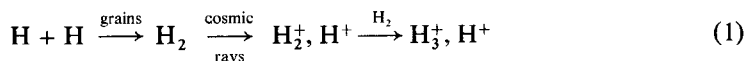
Also included in Table 2 is a list of molecules which have been searched for but not observed at the current levels of detection sensitivity. There is no doubt that as sensitivity levels increase some of these molecules will be detected; indeed CO⁺ was on this list until its recent detection. Several heterocyclic ring compounds (e.g. pyrrole (C₄H₄N) and furan (C₄H₄O), Kutner *et al.*, 1980) are also in this list, highlighting the fact that so far no cyclic compounds have been detected in interstellar clouds.

Ion-chemical models

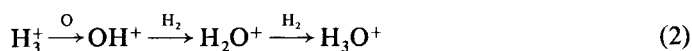
During the last ten years much thought has been devoted to the modes of synthesis of interstellar molecules and this continues as the broader aspects of the subject attract the interest of astronomers, spectroscopists, kineticists and theoreticians. That scientists from these and other disciplines are joining forces to tackle the intriguing and exciting problems in this area of science is well illustrated by the papers contained in the recent conference proceedings on 'Interstellar Molecules' (ed. B. H. Andrew, 1980). The basis of all the ion-chemical models of interstellar molecular synthesis stems from the pioneering work of Solomon and Klemperer (1972), Herbst and Klemperer (1973), Black and Dalgarno (1973a,b), Watson (1973, 1974a,b) and Glassgold and Langer (1975), supplemented by later work by some of these authors (*see e.g.* reviews by Dalgarno, 1975; Dalgarno and Black, 1976; Watson, 1976, 1977; Herbst and Klemperer, 1976a,b). We describe here the essential elements of these earliest models and discuss the most recent developments in Section 4 in the light of the wealth of recent laboratory data.

At the onset, it should be noted that the earliest models were constructed without the relatively large quantity of relevant reaction rate data now available. Thus they were, to a significant extent, based on intuition and inspiration and, as we shall see, have largely stood the test of laboratory checks in as far as these have been possible. We discuss first the basic models of dense clouds.

The major constituent of *dense clouds* is H₂. This presents the greatest problem for gas phase molecular synthesis, since no gas phase mechanism can quantitatively account for the large concentrations of H₂ and so dust grain catalysis has to be invoked for its production. To quote from Dalgarno (1980), 'the existence of H₂ is the strongest evidence of the importance of grain chemistry and the existence of HD is the strongest evidence of the importance of gas phase chemistry'. Ionization is created in the dense clouds by the action of galactic cosmic rays predominantly on H₂ producing H⁺ and H₂⁺. The secondary reaction of H₂⁺ with H₂ is known to proceed rapidly to produce H₃⁺ (a most important precursor ion in the production of other molecules):



Since H₃⁺ and H⁺ do not react rapidly with the abundant H₂ then they are available to react with less abundant but reactive species such as C, N and O atoms. H₃⁺ reacts with O atoms by transferring a proton (Fehsenfeld, 1976) and the OH⁺ product rapidly reacts with H₂ to produce H₂O⁺ which then reacts with H₂ to produce H₃O⁺, an unreactive ion with H₂ (Kim, Theard and Huntress, 1975a):



A parallel route to H_3O^+ , starting from H^+ , begins with the near-thermoneutral reaction (Fehsenfeld and Ferguson, 1972):



Sequential reactions with H_2 again generate H_3O^+ :

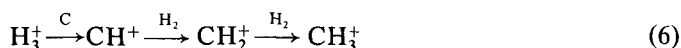


Since (3) is slightly endoergic, it will only be important in diffuse clouds; in cold dense clouds sequence (2) is expected to be the more important route to H_3O^+ . The process of dissociative recombination with the ambient electrons is usually invoked to produce neutral fragment molecules:



These recombination reactions are known to have large rate coefficients but their product distributions are not known. However it is clear that the reaction sequences (1) to (5) will lead to the production of both OH and H_2O . Since this recombination process is often invoked in interstellar chemistry, we discuss it briefly on page 299.

H_3^+ ions can also transfer protons to C atoms, initiating the reaction sequence:



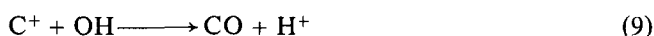
Whilst the first step has not been observed in the laboratory the second and third have and they are very fast (Kim *et al.*, 1975a; Smith and Adams, 1977a,b). Thus (6) can yield the important interstellar ion CH_3^+ which reacts only slowly with H and H_2 in interstellar clouds (page 290) and which can therefore react with minor neutral species resulting in the formation of several observed interstellar molecules. Another, perhaps more efficient, route to carbon containing molecules begins with C^+ ions. Free C atoms can be ionized directly by cosmic rays to produce C^+ but the major source of C^+ is probably the reaction sequence:



The importance of this sequence stems from the large cosmic abundance of He and the large relative abundance of CO in interstellar clouds. Amongst the reactions which can lead to CO production is the associative ionization reaction of CH with O atoms which produces HCO^+ (MacGregor and Berry, 1973; Dalgarno *et al.*, 1973a,b) from which CO is formed by dissociative recombination:



However recent laboratory measurements have shown that HCO^+ is only a very minor product channel in the associative ionization reaction (Vinckier, 1979; Messing *et al.*, 1980) and therefore (8) can only be a minor source of interstellar CO. The CH radicals can be generated following dissociative recombination of CH_2^+ or CH_3^+ ions (formed via (6)). Another possible route to CO is the reaction:



the OH being generated via (5). Clearly which is the largest source of C^+ depends on the proportion of carbon which exists as free atoms to that which is combined in molecules including CO.

Following the precedent set by Bates and Spitzer (1951) who suggested that CH^+ would be formed in diffuse interstellar clouds via the radiative association reaction



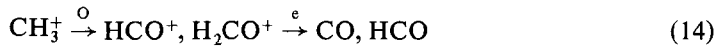
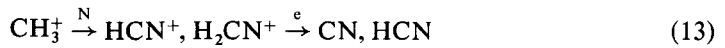
Black and Dalgarno (1973b) proposed that the analogous reaction



would occur in dense clouds in which H_2 is much more abundant than H. A recent calculation by Herbst, Schubert and Certain (1977) has indicated that (11) proceeds via an electronically excited state of CH_2^+ with a short radiative lifetime and this results in a calculated rate coefficient of $\sim 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ a significant magnitude for reactions involving the abundant H_2 . Indirect laboratory evidence obtained from the study of the analogous ternary association reaction tends to support this estimate (page 290). Thus (11) will be an important step in the production of hydrocarbon ions:



which can then react with N and O atoms to give other simple polyatomic species (Dalgarno, 1975; Fehsenfeld, 1976), e.g.:



The synthesis of the larger polyatomic molecules is then expected to proceed via further sequential ion-molecule reactions involving these relatively simple molecules as reactants. This probably involves many reaction steps; however on pages 289–295 we discuss the process of radiative association which, it is postulated, can yield relatively large molecules in a single reaction, especially in low temperature dense clouds.

The initial reactions in dense clouds represented by the simple ion chemistry described above are summarized in the ion-chemical scheme in Fig. 1. More detailed models involving many more sequential and parallel reactions have been given in previous papers (see, for example, Dalgarno, 1975). In Section 4 we discuss some additions which have to be made to the models as a result of recent laboratory work.

Diffuse cloud ion-chemical models involve many of the elements contained in the dense cloud schemes described above. However, there are important differences due to the different physical conditions within and compositions of the clouds. The presence of destructive electromagnetic radiation in diffuse clouds is a crucial factor (not present in the dense clouds) which results in continuous photodissociation of the ambient molecules and this loss rate has to be included in the ion-chemical schemes. Thus, a substantial fraction of all elements exists in the atomic form (including hydrogen) and atoms must therefore play a central rôle in the ion chemistry. As mentioned in Section 2, photoionization of carbon ensures that C^+ will be an important primary ion at least in the outer parts of diffuse clouds. In the inner regions where the ultraviolet radiation is weaker, cosmic radiation will become relatively more important in generating ionization and the major primary ions will again become H^+ and H_2^+ .

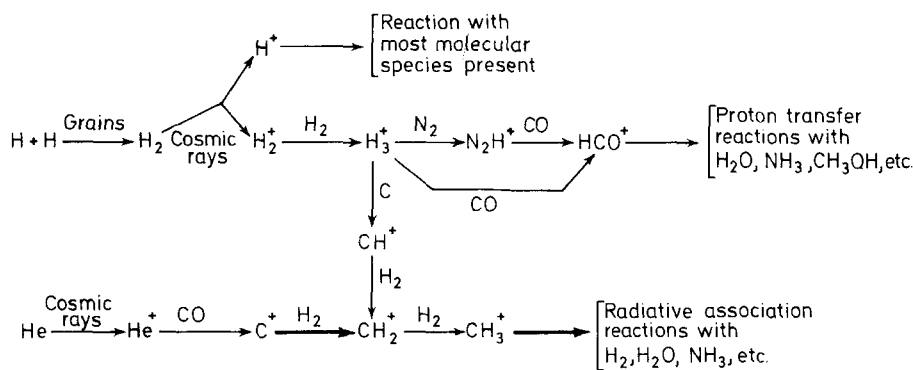
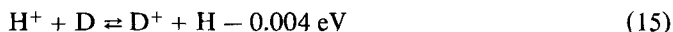


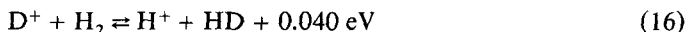
FIG. 1. Some initial ion-neutral reactions in dense interstellar clouds. The steps involving radiative association are indicated by the thick lines. Some extensions to this simple scheme are discussed in the text.

The large fraction of atomic hydrogen present allows the relatively inefficient radiative association reaction (10) to proceed at a significant rate converting C^+ to CH^+ . A recent calculation of the rate coefficient for (10) gives a value of $\sim 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ (Giusti-Suzor, Roueff and van Regemorter, 1976) which is beyond the scope of laboratory measurement and so we are entirely dependent on theory here. However, the calculated rate coefficient is probable accurate to a factor of 2 or 3 and can be used with confidence in model calculations. Since H and H_2 are present in comparable proportions in diffuse clouds, the analogous reaction (11) producing CH_2^+ will be occurring in parallel with (10) and is probably more important in most cases by virtue of its larger rate coefficient (the temperature dependence of the rate coefficients for (10) and (11), as for all other reactions, must also be considered; see pages 286 to 294. The CH^+ and CH_2^+ ions so produced can then react with H_2 in accordance with (6) producing CH_3^+ and all these simple hydrocarbon ions can react with other ambient species including N and O atoms (producing the strong bonded CN and CO groups).

Where H^+ is an important primary ion and where the temperature is high then, as mentioned above, the slightly endoergic charge transfer reaction (3) will generate O^+ ions and thus initiate the sequence of reactions (4) and (5) which result in OH and H_2O . An important reaction sequence which generates the HD observed in diffuse clouds involves another near-thermoneutral reaction:



followed by the isotope exchange reaction



The ergicities, for reactions (15) and (16) control the position of their equilibria at low temperatures. We shall discuss the latter reaction and other isotope exchange reactions on pages 294–298.

More thorough qualitative schemes of dense and diffuse clouds have been described in previous reviews (Dalgarno and Black, 1976; Watson, 1976, 1978). We discuss diffuse cloud chemistry further in relation to recent laboratory work on H, N and O atom reactions on page 288.

An especially important development is the recent detailed quantitative modelling of a few specific diffuse clouds. This is possible because of the wealth of observational data on

column densities (concentrations) of atomic and molecular species which has been obtained using the ultraviolet spectrometer on the Copernicus satellite (*see* for example, Morton, 1975, Spitzer and Jenkins, 1975; Snow, 1977) and more recently using the International Ultraviolet Explorer Satellite (Black, 1980). Of note is the quantitative model of the ζ Oph. cloud by Black and Dalgarno (1977). This kinetic model involves some 250 reactions and about 65 molecular species and involves most of the reactions discussed in this section. The basic objective of the model is to predict molecular densities from the ion-chemical scheme using ionization rates, photodestruction rates and laboratory reaction rate data and to compare the model predictions with actual observations of molecular column densities. In general, the kinetic models satisfactorily predict the in-situ molecular concentrations and are therefore strong indicators of gas phase ion chemistry in diffuse clouds. An apparent failure of the model is that it predicts a much lower concentration of CH^+ than is actually observed. However when it is appreciated that the rate coefficient data used in the model are mostly those obtained at room temperature and that the cloud temperatures are $\lesssim 100$ K, then this is a possible source of error since the problem would be alleviated if the rate coefficient for the important reaction



was smaller at gas cloud temperatures than the 300 K (gas kinetic) value which is used in the model. However we have recently measured the rate coefficient for this reaction at 80 K and find it to be equal to the 300 K value. Therefore it is unlikely to differ appreciably from this at lower temperatures and so the CH^+ problem remains.

Quantitative ion chemical models have also been constructed for the diffuse clouds ζ -Per. and o-Per. (Black *et al.*, 1978; Hartquist, Black and Dalgarno, 1978) and γ -Arae (Federman and Glassgold, 1980). An interesting indication from these detailed studies of diffuse clouds is that they appear to consist of cool, dense central cores surrounded by warmer, more tenuous outer regions, illustrating again the pronounced spatial variations within these clouds.

Some computer model calculations of dense clouds have also been constructed but only for 'generalized clouds', since detailed observations of specific clouds are only just becoming available. Snell (1981) has very recently reported the results of a study of the physical and chemical properties of nine dark clouds. Prior to this, Myers *et al.* (1978) reported a detailed study of the density and temperature structure, kinematics and chemistry of the ρ -Oph. cloud which has properties intermediate between dark and molecular clouds. Noteworthy computer models have been developed by Viala and Walmsley (1976), Kuntz, Mitchell and Ginsburg (1976), Iglesias (1977), Mitchell, Ginsburg and Kuntz (1977, 1978), Prasad and Huntress (1980a,b), Suzuki (1980), Huntress, Prasad and Mitchell (1980) and de Jong, Dalgarno and Boland (1980). These models are very complex, involving hundreds of reactions and variously adopt steady state and time dependent approaches. The rate coefficients used are almost invariably (and of necessity) room temperature values and where particular reactions involved have not been studied then their rate coefficients and products are guessed. These models must therefore be relatively crude at present but nevertheless they are valuable contributions to the subject since they can indicate the reactions which are critical in the cloud chemistry and therefore those particular reactions which need to be re-examined and those which need to be studied in the laboratory.

Finally it is instructive to comment on the essential collaborative nature of this subject. Whilst it is obvious that progress in all science is achieved by collaboration and the exchange of ideas, it is especially so in this subject. The astronomical observations of the molecules initiated this field of research and stimulated further interest in the interstellar clouds and as a result an appreciation of the physical conditions within the clouds was

obtained which is important in estimating the rate of cloud collapse to form stars. Laboratory spectroscopists, theorists, chemists and kineticists took up the challenge to provide the critical data on characteristic emission and absorption spectra to facilitate identification of molecular lines and to provide reaction data in support of the chemical models proposed for the synthesis of the observed molecules. The ion-chemical models then predict molecular densities which must compare with actual observations if they are to be credible. Such is gradually being achieved, indicating that the essential elements of the models are valid. As confidence grows in the models, they can be used as indicators of critical chemical reactions which need to be studied in the laboratory and can indicate where existing laboratory rate coefficients need to be re-examined (for example at lower temperatures). They can also be valuable to observational astronomers in predicting molecular species which might exist in interstellar clouds but which have not yet been detected. This close inter-relationship between the various disciplines is represented schematically in Fig. 2. The recent contributions to this overall effort by laboratory kineticists are presented in the next section.

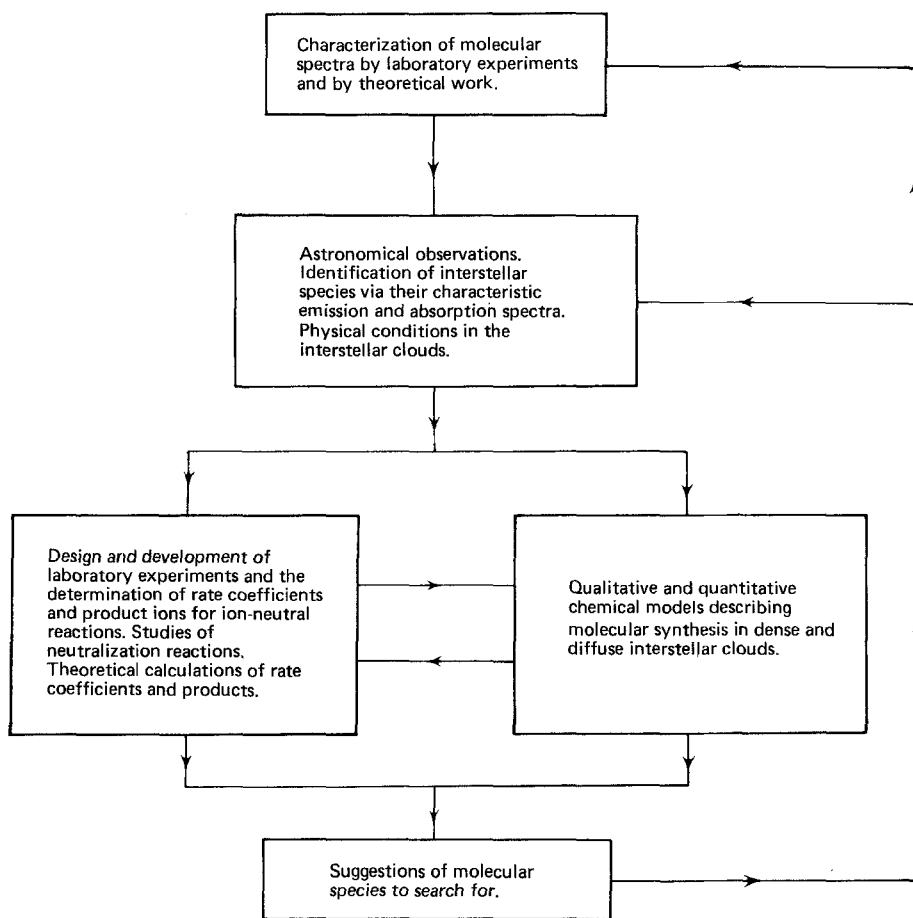


FIG. 2. Schematic description of the inter-relationship between the various contributions to the chemistry and physics of interstellar molecules.

4. RECENT LABORATORY STUDIES OF ION-NEUTRAL REACTIONS

It follows from the above, that a large number of ion-neutral and ion-electron reactions must be occurring to produce the molecules observed in interstellar clouds and ideally the rate coefficients and products for every reaction involved in the ion-chemical models should be determined in the laboratory over the range of cloud temperatures. Unfortunately the experimental techniques for such studies are not yet developed, but considerable progress towards this goal has been made recently as described below. To date, the majority of the data have been obtained at or somewhat above room temperature using the ion cyclotron resonance (ICR) technique (e.g. Henis, 1972) or the flowing afterglow (FA) technique (Ferguson, Fehsenfeld and Schmeltekopf, 1969; Fehsenfeld, 1975b; Smith and Adams, 1979). Some relevant data have been obtained in flowing afterglow down to temperatures of 80 K (e.g. Fehsenfeld *et al.*, 1974a,b). A large fraction of the rate coefficients, k , for reactions of interstellar interest are found to be at the gas kinetic (collisional) limit ($k \sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$; Su and Bowers (1975) and *see*, for example, the data complications of Huntress (1977) and Albritton (1978)) and k for such reactions is generally independent of temperature (Ferguson, 1975). Therefore reactions which are fast at (or near) room temperature will generally be fast at gas cloud temperatures. However, there are exceptions to this general rule (*see* page 287). Reactions that proceed at rates significantly slower than the collisional limit are usually temperature dependent, unpredictably exhibiting either positive or negative temperature dependences. For such reactions, it is obviously dangerous to rely on extrapolations of k over a wide temperature range.

First we briefly discuss the techniques used to determine rate coefficients and product ions, emphasizing the most recent developments, and in the following section, we describe some of the most important data obtained recently for exoergic binary reactions. In the next section we concentrate on the process of radiative association and show how laboratory data on ternary association reactions have been used to support the premise that radiative association is important in molecular synthesis in interstellar clouds. Isotope exchange in ion-molecule reactions is discussed in the following section and recent laboratory data are used to show that isotope fractionation is at least partly responsible for the observed enrichment of rare (heavy) isotopes in interstellar molecules. Finally, a brief discussion is presented of the neutralization processes which have to be invoked to convert molecular positive ions into the observed neutral molecules. At the appropriate places it is indicated, but only in a qualitative fashion, how the new experimental data assist in the improvement and extension of interstellar ion-chemical models.

Recent developments in experimental techniques

Much of the relevant data obtained using ICR techniques have been obtained by Huntress and his colleagues (*see* for example Kim *et al.*, 1974, 1975a,b; Karpas, Anicich and Huntress, 1979; *see also* the review by Huntress, 1977) and those from the FA techniques by Fehsenfeld and Ferguson and their colleagues (Fehsenfeld *et al.*, 1966, 1974a,b; Fehsenfeld and Ferguson, 1972, 1974; Fehsenfeld, 1976), by Bohme and Schiff and their colleagues (Burt *et al.*, 1970; Schiff *et al.*, 1974; Schiff and Bohme, 1979) and by Liddy, Freeman and McEwan (1975) and Freeman, Harland and McEwan (1978). These two techniques are fundamentally very different, the ICR being a low pressure, essential collisionless ion trap experiment, whereas the FA is a relatively high pressure, collision dominated experiment. Experimental evidence presented on page 297 indicates that the ions in ICR cells are suprathreshold thus explaining some of the discrepancies between the

product distributions of some specific ion-molecule reactions as determined in ICR cells and in truly thermalized flow reactors such as the FA or the selected ion flow tube (SIFT). Notwithstanding these remarks, ICR experiments continue to provide a great deal of critical data for determining ion-molecule reaction mechanisms and for establishing relative acidity/basicity scales of gaseous species (Beauchamp, 1975; Bartmess and McIver, 1979).

The FA has been used very successfully (mainly by its originators) to study a large number of positive and negative ion-molecule reactions of relevance to atmospheric ion chemistry (e.g. Ferguson *et al.*, 1979). In essence the technique involves the creation of reactant ions in a fast flowing carrier gas or gas mixture whence the ions are transported downstream. The gas temperature, and hence the ion temperature, can be varied within the range 80 K to 900 K (Lindinger *et al.*, 1974). Reactant gases are added to the carrier gas at selected positions downstream and the loss of reactant ions and the formation of product ions are observed further downstream by a mass spectrometer sampling system. Thus reaction rate coefficients and product ions are determined at truly thermal energies. Many hundreds of reactions have been studied using this technique including some of interstellar significance (*see* the compilation by Albritton, 1978) which will be considered below.

However, the FA cannot be used in a satisfactory manner to study many of the reactions of interstellar significance, such as for example reactions of CH^+ , CH_2^+ ions, for the simple reason that many of the important ions (such as the two cited) react rapidly with their parent gas which is necessarily present in the flow tube. Further, these ions cannot be generated as the only ionic species in the FA and the simultaneous presence of more than one reactant ionic species, together with their parent gas, results in reaction patterns which are far too complex to deconvolute. To avoid these difficulties the SIFT technique has been developed (Adams and Smith, 1976a,b) which has all the attributes of the FA for the study of ion-neutral reactions. However additionally and most importantly, it uses mass filtering to enable a single ionic species (generated together with other ion species in a remote ion source) to be injected into the flowing carrier gas. By this means, the ion parent gas is also excluded from the flow tube thus avoiding complicating secondary reactions. Using the SIFT, many hundreds of reactions of ions of interstellar interest have recently been studied, including both binary and ternary reactions. In principle, virtually any ion-neutral reaction can be studied using this technique. At present, the temperature range available to the SIFT is 80 K to 600 K, although it could be developed to operate close to the temperatures of dense gas clouds. The technique has been described in detail in a recent review (Smith and Adams, 1979).

Finally it is pertinent to mention here two potentially valuable experiments which can operate at temperatures below the present lower temperature limit of the FA and SIFT. One has been developed at the Max-Planck-Institut für Kernphysik at Heidelberg by Arnold and Böhringer and consists of an injected-ion drift tube which can be operated at temperatures as low as 20 K. Preliminary measurements of several ionic reaction rate coefficients at 40 K have revealed no major experimental problems. Indeed, the preliminary work indicates that the apparatus is capable of providing much ion-neutral reaction rate data at these low temperatures.

The other new experiment has been developed at The Joint Institute for Laboratory Astrophysics at Boulder, Colorado by Dunn and his colleagues. This is an ion trap experiment (Walls and Dunn, 1974) which can now be operated down to temperatures below 10 K and is beginning to provide very exciting ion-molecule reaction rate data at these temperatures. We will refer to some of these preliminary data in the next section.

The further exploitation of the low temperature SIFT, together with these two new techniques, will provide new insights into the ion chemistry in interstellar clouds.

Exoergic binary reactions

The objectives of these studies, as they relate to interstellar chemistry, can be categorized approximately as follows:

1. Surveys of the reactions of ions in particular sequences, such as CH_n^+ , NH_n^+ , etc., with known interstellar neutral species in order to identify the important routes to other interstellar molecules. The major interstellar neutrals, especially H_2 and CO , are always included as reactants in these studies since the reactivity of a particular ion with these species largely determines its 'lifetime' in the clouds. Those ions which do not react with H_2 or CO at an appreciable rate (e.g. C^+ , HCO^+ , NH_4^+ , H_3CO^+), we loosely call 'terminating ions' and they are candidates for radiative association reactions (*see next Section*).
2. Temperature dependence studies of those reactions which are considered to be important in ion-chemical models and which are slow at room temperature. Extrapolation of room temperature data is now known to be unacceptable in several important cases and has led to some misleading conclusions regarding the ion-chemical routes to interstellar molecules.
3. Studies directed towards gaining an understanding of a particular cloud or cloud type. For example, studies of ion-atom reactions have been directed especially towards diffuse cloud chemistry.
4. Studies directed towards specific problems in interstellar chemistry such as how are the cyanopolyacetylenes synthesised, identifying the initial reactions in the synthesis of sulphur-containing molecules, why have no chlorine-containing molecules been detected, and why ion-chemical models underestimate the concentration of CH^+ in diffuse clouds.

We will now discuss some recent results of such studies.

Detailed studies of the reactions of ion sequences have been carried out using the SIFT. These have included ions in the series, CH_n^+ ($n = 0$ to 4) (Smith and Adams 1977a,b,c., 1978a,b; Adams and Smith 1977, 1978), C_2H_n^+ ($n = 0$ to 4) (Adams and Smith, 1977; Smith and Adams, 1977c), H_nCO^+ ($n = 0$ to 3) (Adams, Smith and Grief, 1978), N_n^+ ($n = 1$ to 4), O^+ , O_2^+ and NO^+ (Smith, Adams and Miller, 1978a), NH_n^+ ($n = 0$ to 4) (Adams *et al.*, 1980; Smith and Adams, 1980b, 1981a), H_nS^+ ($n = 0$ to 3) (Smith, Adams and Lindinger, 1981a), and C_2H_n^+ ($n = 0$ to 7) with HCN (Mackay *et al.*, 1980). Also many reactions of CH_n^+ , C_2H_n^+ and C_2N^+ have been studied in SIFT and FA experiments (Schiff and Bohme, 1979; Schiff *et al.*, 1980). Some of the individual reactions in these series had been studied previously in the ICR (*see the compilation of Huntress, 1977*) and the FA (Liddy *et al.*, 1975; Freeman *et al.*, 1978). The majority of these ion-molecule reactions proceed at or near the gas kinetic limit (Su and Bowers, 1975) and the products demonstrate the wide variety of reaction mechanisms which can occur, including simple charge transfer, dissociative charge transfer and proton transfer. For those reactions between ions with large recombination energies (e.g. N^+ , CO^+) and polyatomic molecules, multiple fragmentation channels are often evident. Prediction of the product distributions for such reactions is 'beyond the state of the art' at present and emphasizes the importance of the experiments. Fortunately, the product distributions for most appreciably-exoergic binary reactions do not change markedly with temperature over the limited range from 300 K down to 80 K (and presumably down to cloud temperatures). However near-thermoneutral reactions can be influenced greatly by temperature changes (pages 295–298). Reactions which are usually more predictable are those between ions which can be considered as simple protonated molecules, such as HCO^+ and N_2H^+ , and more complex

molecules of large proton affinity. Such reactions often proceed rapidly by direct proton transfer:

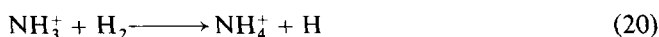


Reaction (18) is important in interstellar clouds since it has a controlling influence on the concentrations of N_2H^+ and HCO^+ , which are both observed interstellar species (Herbst *et al.*, 1975). Detailed studies of proton transfer reactions have been carried out by Bohme and his colleagues (e.g. Bohme, 1975; Tanner *et al.*, 1979). Proton transfer is also an effective 'neutralization' process (*see* page 300).

A likely solution to a major problem in interstellar chemistry has emerged from these recent detailed surveys and illustrates the dangers of extrapolating rate data to low temperatures. For some years, it was not understood how NH_3 could be formed via gas phase ion chemistry. It was considered (Herbst and Klemperer, 1973) that the sequence of reactions:



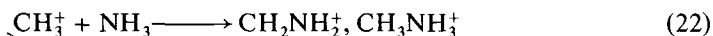
would proceed rapidly under cloud conditions, but the next critical step:



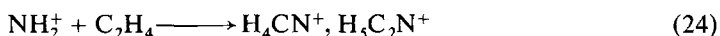
which generates NH_4^+ (after recombination with a free electron this presumably produces NH_3) was thought to be too slow at cloud temperatures to represent a significant production of NH_3 . $k(20)$ at cloud temperatures was deduced by extrapolation of the data of Fehsenfeld *et al.* (1975) which was obtained above 300 K and indicated that $k(20)$ decreased exponentially with decreasing temperature. Recent studies of (20) by Smith and Adams (1981a) have shown that $k(20)$ does not decrease greatly as the temperature is reduced from 300 K to 80 K ($k(20) \sim 2(-13) \text{ cm}^3 \text{ s}^{-1}$) a result also obtained by Fehsenfeld (private communication). Also, a very recent study by Luine and Dunn (private communication) at a temperature of about 4 K, indicates that $k(20)$ has actually increased above the 80 K value to about $6(-12) \text{ cm}^3 \text{ s}^{-1}$. Thus the bottleneck which (20) had apparently presented for some years was never real. Further, the survey of the NH_n^+ reactions showed that NH_3^+ ions rapidly abstracted H atoms from most hydrogen-containing molecules, so the presence of significant concentrations of, for example, CH_4 , C_2H_4 , C_2H_2 , etc., provides additional pathways for NH_4^+ production (Adams and Smith, 1980a). Another potential problem in the sequence of reactions (19) is that the first stage is probably close to thermoneutral and may even be somewhat endoergic which could have implications to low temperature interstellar cloud chemistry. However, our SIFT studies have shown that the rate coefficient for this reaction ($\text{N}^+ + \text{H}_2$) is not measurably smaller at 200 K than it is at 300 K and this suggests that if the reaction is endoergic it is only slightly so ($\Delta H \lesssim 5 \text{ meV}$). Thus, whilst this reaction could be slower at interstellar cloud temperatures than was previously thought, it should not seriously diminish the rate of NH_4^+ production and (20) should still be the slowest reaction in the NH_4^+ production sequence.

Many other important and interesting conclusions can be drawn from the very large amount of data now available on binary reactions. For example, it is clear why so many of the molecules observed in interstellar clouds are cyano- and amino-compounds (*see* Table 2) and why so few are nitroso-compounds (Adams and Smith, 1980a). The mass of data

indicates that many ion chemical routes lead to the production of molecules containing the strongly bonded, $-\text{CN}$ and $-\text{NH}$ groups. For example, the important interstellar ions C^+ and CH_3^+ react with NH_3 thus :



Also the reactions of ammonia-derived ions with hydrocarbons produce ions containing $-\text{CN}$:



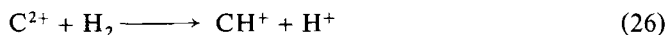
Neutralization of the product ions of (21) to (24) can lead to the observed species CN , HCN , CH_2NH and CH_3NH_2 . Conversely, from the many hundreds of reactions studied which involve likely interstellar ions and molecules, it is rare to find a reaction which produces ions containing the $-\text{NO}$ group. One example is:



which can lead to NO and HNO , the only $\text{N}-\text{O}$ bonded species so far detected in interstellar clouds. Reactions of the kind (21) to (25) can now be confidently included in comprehensive models of dense interstellar clouds to extend limited schemes such as that represented in Fig. 1. Such detailed schemes have been presented recently (e.g. Mitchell, Ginsberg and Kuntz, 1978).

In Section 3, it was noted that reactions of ions with atoms, especially H , N and O , were important in diffuse clouds. Laboratory studies of ion-atom reactions present experimental difficulties; the problem is to generate adequate concentrations of atoms in reaction cells and to determine their concentrations. The earliest relevant studies of H and O atom reactions were carried out in a FA by Fehsenfeld and Ferguson (1971, 1972) and these studies were later extended to reactions of N atoms (Fehsenfeld, 1976). These included the important near-resonant reaction (3) between H^+ and O , and the reactions of H_3^+ with O and of CH_3^+ with O and N . Recently, Karpas *et al.* (1979) using an ICR, have studied the reactions of several ions with H and D atoms and found that H_2^+ , N_2^+ and HCN^+ reacted with both H and D atoms but that CH_n^+ and C_2H_n^+ ($n = 2$ to 4) did not react with either H or D atoms. Viggiano *et al.* (1980) studied the reactions of CH^+ , CH_2^+ , CH_3^+ , C_2^+ , C_2H^+ , C_2H_2^+ , H_2O^+ and D^+ with N and O atoms using a SIFT. These data showed again the great propensity for the formation of the strongly-bonded $-\text{CN}$ and $-\text{CO}$ groupings, which are such common groupings in interstellar molecules (Table 2).

We have included many of these atom reactions in the limited ion-chemical model of diffuse interstellar clouds shown in Fig. 3. Note how the oxygen is channelled into HCO^+ which, following recombination with electrons will produce the ubiquitous CO . Similarly, the nitrogen is combined into cyanide-bearing molecules. Thus, the qualitative aspects of the ion chemistry of diffuse clouds are clear and, as we discussed on page 282, quantitative diffuse cloud models satisfactorily predict the observed concentrations of most species. A notable exception is CH^+ for which the models predict a smaller concentration than is observed and this could indicate an additional source of CH^+ . Dalgarno (1976) and Langer (1978) suggested that such a source might be the reaction:



SIFT data obtained for the reactions of other doubly-charged ions with H_2 (Adams *et al.*, 1979; Smith *et al.*, 1979; Adams and Smith, 1980b) suggested that CH^+ would not be a likely product of (26). This reaction has since been studied in a SIFT and it was found that

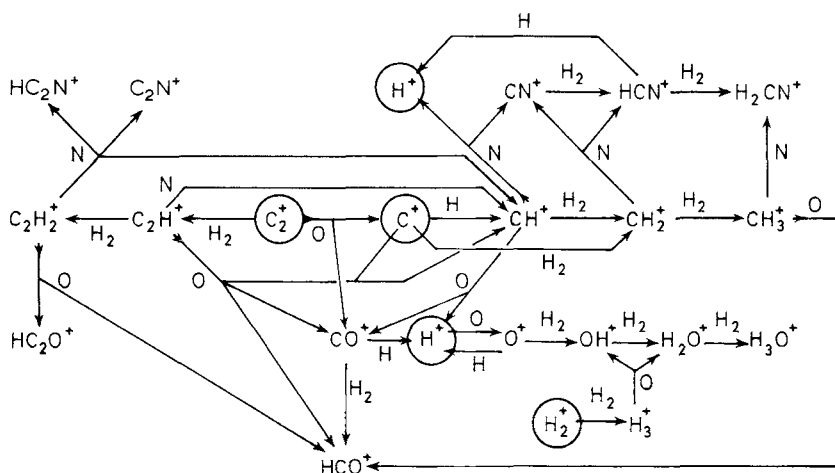
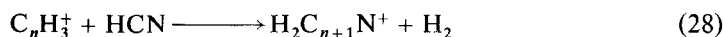


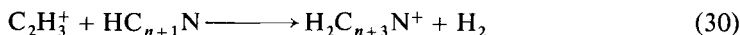
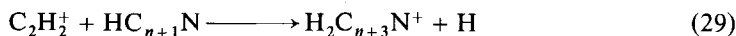
FIG. 3. A limited ion-chemical scheme for diffuse interstellar clouds. The ions which are circled are formed primarily via ultraviolet and cosmic ray ionization of the corresponding neutral species.

H^+ and C^+ were the major products and that no CH^+ was produced; so the CH^+ problem remains unresolved (Smith and Adams, 1981a).

Finally in this section, we consider an interesting problem in dense cloud chemistry; how the cyanopolyacetylenes are formed. To date HC_3N , HC_5N , HC_7N and HC_9N have been detected in dense clouds following the determination of their spectra in laboratory experiments and by calculation (Alexander, Kroto and Walton, 1976; Kirby, Kroto and Walton, 1980; Broten *et al.*, 1978). Schiff and Bohme (1979) have sought a solution to this problem by studying the reactions of several hydrocarbon ions with HCN (*see also* Freeman *et al.*, 1978; Mackay *et al.*, 1980; Schiff *et al.*, 1980). From their laboratory observations they suggest the following general schemes for the formation of cyanopolyacetylenes:



where n is even. The formation of the $C_nH_2^+$ and $C_nH_3^+$ ions in dense clouds has been described previously (Watson, 1974a,b; Dalgarno and Black, 1976; Smith and Adams, 1977c). The $HC_{n+1}N$ neutral molecules are formed following electron dissociative recombination of the product ions in (27) and (28). These neutrals can then undergo further reaction with $C_2H_2^+$ and $C_2H_3^+$ building larger members of the series thus:



This rather appealing qualitative solution to the problem must however be substantiated by further laboratory experiments before it, in common with proposed routes to other species, can be confidently adopted in the detailed quantitative models of the chemistry of dense clouds which are now being constructed (e.g. Prasad and Huntress, 1980a,b; de Jong, Dalgarno and Boland, 1980).

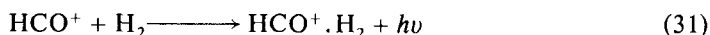
Exoergic binary reactions, of potential importance to interstellar ion chemistry, will be studied for some time to come at least until the key reactions, as identified by present and

future quantitative models, have been thoroughly investigated at appropriately low temperatures.

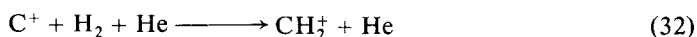
Radiative association

In Section 3 we discussed the importance of the ion–neutral radiative association reactions of C^+ with H and H_2 (reactions (10) and (11)) in the initial stages of molecular synthesis. In this section, we expand on this theme and present evidence, obtained from laboratory studies of ternary association reactions, which indicates that radiative association will be an efficient and effective single stage process for the synthesis of larger interstellar molecules.

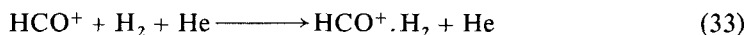
Estimates of the radiative association rate coefficients, k_R for (11) and for:



were made by Fehsenfeld *et al.* (1974a) from their FA studies of the rate coefficients, k_3 , of the corresponding analogous collisional association reactions:



and



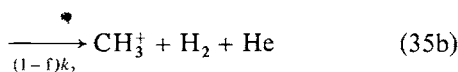
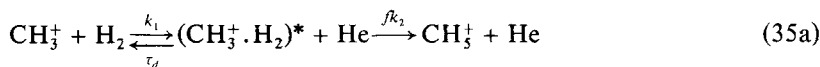
Even at 90 K, (32) and (33) were very slow, as has been confirmed by recent SIFT measurements (*see later in the section*). Estimates of k_R for the equivalent radiatively stabilized reactions were obtained using the procedure described below (k_R (11) ~ 4 – 17) $\text{cm}^3 \text{s}^{-1}$ and k_R (31) ~ 1 – 18) $\text{cm}^3 \text{s}^{-1}$). This value of k_R (11) is about 3 orders of magnitude smaller than the value calculated by Herbst *et al.* (1977), this large discrepancy being mainly due to the different radiative lifetime, τ_R , (*see below*) adopted for the $(CH_2^+)^*$ excited intermediate complex. Fehsenfeld *et al.* used a value of τ_R of 10^{-2} s which is appropriate to transitions between vibrational levels; however, Herbst *et al.* showed that the association proceeds via an electronically excited state with a τ_R of about 10^{-5} s. Subsequently, Herbst (1976) calculated k_R for the reactions of HCO^+ , CH_3^+ , H_2CN^+ and H_4CN^+ with H_2 . These reactions were chosen as possible candidates for radiative association in interstellar clouds since they do not proceed at a measurable rate via the normal binary fragmentation channels and therefore association is the only other possible reaction. These first calculations indicated that, in all cases, k_R was so small that radiative association would not be very important for these reactants even at the low temperatures and relatively high H_2 densities pertaining to dense interstellar clouds.

However, during the early SIFT studies at 300 K of the reactions of the methane-derived ions CH_n^+ (Smith and Adams, 1977a), it was observed that CH_3^+ undergoes rapid collisional association reactions with several molecular gases at 300 K, including the abundant interstellar molecules H_2 and CO. The association of CH_3^+ with H_2O was especially rapid, and with NH_3 , H_2CO , CH_3OH and CH_3NH_2 (all interstellar species) the association channels were so fast that they competed with parallel binary fragmentation channels (Smith and Adams, 1977b; Adams and Smith, 1978). From these observations, it follows that the excited intermediate complexes which form in these collisions must have long lifetimes, τ_d , against unimolecular decomposition, since the stabilization frequency by gas atoms in the reaction cell was quite small. It was therefore considered that these reactions would be prime candidates for radiative association in

interstellar clouds. The following considerations, coupled with the growing body of laboratory data, apparently substantiate this view. We use the CH_3^+ reaction with H_2 to illustrate the relationship between collisional association and radiative association. The overall collisional association reaction is:

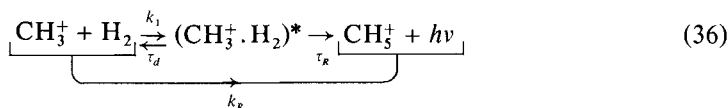


This can be considered to proceed via the excited intermediate complex $(\text{CH}_3^+ \cdot \text{H}_2)^*$ which in collision with a helium atom can either be stabilized to CH_3^+ or dissociated back to the reactants:



k_1 and k_2 are the gas kinetic rate coefficients (usually calculated using the theory of Su and Bowers, 1975) for the CH_3^+/H_2 and $(\text{CH}_3^+ \cdot \text{H}_2)^*/\text{He}$ collisions respectively, and f is the fraction of the collisions with He which result in stabilization. It is readily shown by a simple kinetic analysis (Ferguson, 1972; Smith and Adams, 1978a) that the overall ternary rate coefficient, k_3 , can be equated to $k_1 k_2 f \tau_d$. Thus by measuring k_3 , τ_d can be obtained. In the high pressure limit the reaction becomes pressure independent, that is it exhibits binary kinetics with a rate coefficient equal to $k_1 f$. Under these circumstances, only a lower limit to τ_d can be obtained. Several CH_3^+ association reactions exhibited binary kinetics at the lowest pressures (~ 0.1 Torr) at which SIFT experiments can be currently operated (Smith and Adams, 1978a) and in one reaction (with HCN, *see below*) such is observed even at the much lower ICR pressures. These observations imply either a large τ_d or a short radiative lifetime, τ_R , for the excited intermediate complexes.

The analogous radiative association reaction can be represented thus:



Again a simple kinetic analysis relates k_R to τ_d and τ_R thus:

$$k_R = k_1 \frac{\tau_d}{\tau_d + \tau_R} \approx k_1 \frac{\tau_d}{\tau_R} \text{ when } \tau_R \gg \tau_d \quad (37)$$

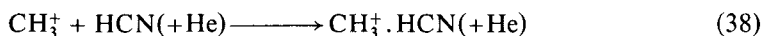
Hence an estimate of τ_d from laboratory data, and a knowledge of τ_R , provides an estimate for k_R . Values of τ_R for these complexes are not available and the usual approach is to follow the guidelines given by Herzberg (1967) and adopt a value of $\sim 10^{-3}$ s to obtain estimates of k_R . The original estimates obtained from the 300 K laboratory data indicated that, even at this relatively high temperature, radiative association could proceed at appreciable rates in some reactions (Smith and Adams, 1977c). Also they would be expected to become increasingly rapid as the temperature is decreased (Herbst, 1976). Several of the CH_3^+ reactions were re-examined at the lower temperature of 225 K (the lower limit of temperature available to the original SIFT) and the expected increase in k_3 was observed (Smith and Adams, 1978a). Thus, by assuming a power law dependence of k_3 with temperature of the form $k_3 \sim T^{-n}$ as predicted by the RRKM theory (*see* Herbst, 1976), it was possible to obtain a better estimate of k_R at interstellar cloud temperatures

(Smith and Adams, 1978b). The rapid changes of k_3 (and hence k_R) with temperature ($n \sim 3$ to 5) were however much greater than predicted by the theory of Herbst and further emphasized the likely importance of radiative association at low temperatures. Later measurements of k_3 for the same CH_3^+ reactions, but over a wider temperature range (Adams *et al.*, 1979), confirmed the power law dependence on temperature, but due to temperature calibration errors in these experiments, the n values were somewhat over-estimated. The very recent measurements of k_3 for several CH_3^+ and CD_3^+ association reactions (Adams and Smith, 1981b), over the wide temperature range of 80 K to 550 K and in which great care was taken to ensure that the temperature measurements were accurate, have established the validity of the power law over the temperature range investigated. These latest measurements indicate n to vary from about 2.5 (for diatomic reactant gases) to about 3.5 (for polyatomic reactant gases) in good agreement with the most recent predictions of Herbst (1979a) from his statistical theory of ternary association reactions. Also, very recently Herbst (1980) has revised his original theory of radiative association in a thorough new look at this process and concludes that certain radiative association reactions occur rapidly at low temperatures and are probably important in the synthesis of complex interstellar molecules. The growing interest in this subject has seen the appearance of other important theoretical studies of these collisionally and radiatively stabilized reactions (Bates, 1978, 1979, 1980).

The major uncertainties in deriving k_R from temperature dependent studies of k_3 results from the need to deduce k_3 at very low temperatures from extrapolated curves which describe the data obtained above 80 K, and the need to assume a value of τ_R . Herbst (1979b) has noted that in the $\text{C}^+ + \text{H}_2$ reaction k_R should depart from the power law (increase less steeply) for temperatures below 50 K and that extrapolations of data for other reactions to 20 K will probably over-estimate τ_d and hence k_R . Preliminary laboratory data are available for the reactions $\text{N}_2^+ + 2\text{N}_2 \rightarrow \text{N}_4^+ + \text{N}_2$ and $\text{O}_2^+ + 2\text{O}_2 \rightarrow \text{O}_4^+ + \text{O}_2$, which indicate that k_3 does indeed increase less rapidly for these reactions below about 80 K (Böhringer, private communication). However, it appears that τ_d will not be over-estimated by more than a factor of about 2 at cloud temperatures due to this phenomenon. However, to mitigate the effect of these small τ_d values on k_R , there is evidence available from spectroscopic experiments (Dujardin *et al.*, 1980) which strongly suggests that the 10^{-3} s estimate for τ_R may be too large. In these experiments relaxation times of low lying vibrationally excited levels in some polyatomic molecules have been determined to be as short as 10^{-6} to 10^{-5} s, and vibrational relaxation from the higher vibration levels which are populated in excited complexes formed in association reactions, is expected to be even more rapid than from low lying levels (Leach, Dujardin and Taieb, 1980). Clearly the smaller τ_R , the larger k_R and thus the more important the process of radiative association.

Because of its relevance to interstellar chemistry further extensive studies have been made of the ternary association reaction (32) and, from the k_3 obtained, estimates have been made of k_R for the analogous radiative association reaction (11). The studies include those of Fehsenfeld (1980), Smith and Adams (1980c), Johnsen, Chen and Biondi (1980) and Adams and Smith (1981b). These studies indicate that k_3 varies as $T^{-1.3}$ in accordance with theoretical predictions (Herbst, 1979a), and the estimates obtained for k_R lie within the range 10^{-16} to 10^{-14} $\text{cm}^3 \text{ s}^{-1}$ depending on the assumed value for τ_R . These estimates are in acceptable agreement with the theory (referred to on page 280).

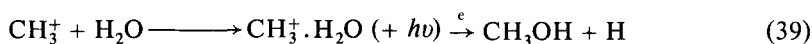
A most impressive example of rapid (collisional) association has been observed in the reaction:



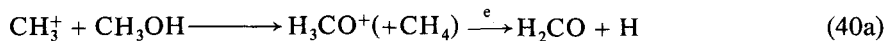
by Vlachos *et al.* (1979) using a SIFT. This reaction exhibits binary kinetics over the usable pressure range of the experiment with an equivalent binary rate coefficient of 2 (–9)

$\text{cm}^3 \text{s}^{-1}$ at 300 K, i.e. near the gas kinetic value. Even more impressive is that in an ICR experiment, McEwan *et al.* (1980) have observed the association reaction of CH_3^+ with HCN to be pressure independent within the range 10^{-6} to 10^{-2} Torr, but with a much smaller rate coefficient of 2 ± 1 (-10) $\text{cm}^3 \text{s}^{-1}$ than that obtained with the SIFT. However, the ions in the ICR cell are thought to be suprathreshold which could explain the large difference between the SIFT and ICR rate coefficients for this reaction since an increase in temperature would presumably reduce τ_d . Nevertheless the remarkable results for this reaction indicate that τ_d for the $(\text{CH}_3^+ \cdot \text{HCN})^*$ complex must be very long or alternatively that τ_R must be very short. In either case, this association reaction must surely proceed with unit efficiency in interstellar clouds (presumably ultimately resulting in CH_3CN , an observed species). It is interesting to note that rapid binary association between Li^+ ions and several polyatomic hydrocarbons has also been observed in low pressure ICR experiments (Woodin and Beauchamp, 1979).

Finally in this section, it is pertinent to discuss two problems in interstellar molecular synthesis to which radiative association offers a possible solution. To explain the formation of H_2CO via gas phase ion chemistry has been particularly troublesome (Watson, 1976) and so grain surface catalysis has been proposed as an alternative formation mechanism (Watson, Crutcher and Dickel, 1975). The recent observation of HDCO (Langer *et al.*, 1979), however, moved the focus of attention back to gas phase solutions for its formation. A possible reaction scheme involving radiative association had previously been proposed by Smith and Adams (1978c) which stemmed from their detailed studies of collisional association reactions of CH_3^+ in the SIFT. The first stage involves the formation of CH_3OH :

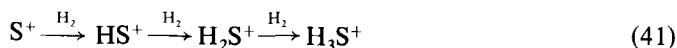


Secondly, the CH_3OH reacts with CH_3^+ :



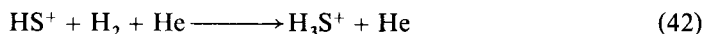
The fragmentation branch (40a) is an 80 per cent product of the reaction and leads to H_2CO . The product of (40b) could either be $(\text{CH}_3)_2\text{O}$ or $\text{C}_2\text{H}_5\text{OH}$ which are both observed interstellar molecules (Table 2). It is interesting, and perhaps very significant, that in interstellar clouds the relative concentrations of the molecules involved in this simple scheme are in the order $[\text{H}_2\text{O}] > [\text{CH}_3\text{OH}] > [\text{H}_2\text{CO}]$, consistent with the requirements of the scheme. Also, in a detailed study of methyl alcohol in 14 gas clouds, Gottlieb *et al.* (1979) conclude that the reaction of CH_3^+ with H_2O leading to CH_3OH is consistent with their observations and that the notion that the observed CH_3OH and H_2CO are intimately connected though their chemistry is, at least, not contradicted by their observations. Further support for the occurrence of radiative association in interstellar clouds is obtained when the chemistry of C^+ and CH_3^+ with H_2 and NH_3 is considered with reference to the Sgr.B2 and Orion clouds (Smith and Adams, 1977c).

Another difficulty in ion-chemical models is in explaining how the observed H_2S is synthesized. The problem arises when it is appreciated that the reactions in the sequence:



are all endoergic for ground state reactants. However, the reaction of metastable S^+ (^2D ,

²P) with H₂ is fast and generates HS⁺ (Tichy *et al.*, 1979; Smith and Adams, 1981a). Also it has been observed (Smith and Adams, 1981a) that the association reaction:



is sufficiently rapid at 80 K to indicate that the analogous radiative association reaction will be able to convert the HS⁺ to H₃S⁺ in interstellar clouds. The viability of such a mechanism for the production of H₃S⁺ (and H₂S following electronic recombination) depends on whether an adequate concentration of metastable S⁺ can be formed in interstellar clouds and also if its lifetime against radiative decay is long enough to allow a significant proportion to undergo collisions with H₂ molecules. A positive argument is presented in favour of this mechanism in a recent paper (Smith and Adams, 1981a).

From the evidence presented here, it does appear likely that radiative association reactions, especially those involving polyatomic species, will play an important rôle in the synthesis of large molecules in interstellar clouds. Many ions and neutrals could be involved and a large number of possible ion-neutral reactions have been proposed as candidates for radiative association (*see for example*, Huntress and Mitchell, 1979). It is also pertinent to note that radiative association between large neutral species was proposed several years ago by Williams (1971) and more recently between small radical species (H, OH, NH₂, etc.) by Field, Adams and Smith (1980). It is the extremely low temperatures within interstellar clouds which could make such processes viable. Under such conditions, macromolecules could probably be formed by a sequence of radiative association reactions and may even initiate the growth of dust particles.

Isotope exchange reactions

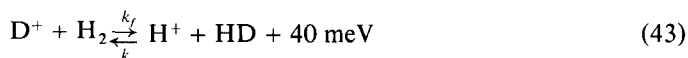
Isotopic labelling of reactants has long been used to trace the paths of exoergic ion-neutral reactions, especially in ion beam experiments (*see the recent review by Gentry, 1979*) and in ICR experiments (e.g. Huntress and Elleman, 1970; Kim and Huntress, 1975; Smith and Futrell, 1977). It is assumed that the course of such reactions (i.e. the rates coefficients and products) is not significantly dependent on the isotope involved. Also recently, it has been shown (Smith and Adams, 1980b) how isotopic labelling of either or both of the reactant ion and reactant neutral can be used to determine the identity of the product ions in ion-molecule reactions in which two or more product ions have the same mass. In this section, however, we are largely concerned with isotope exchange reactions which are in the normal sense thermoneutral and in which only zero-point energy differences between reactants and products and statistical factors control the course of the reactions. Examples of such reactions are (15) and (16), and it has also been previously mentioned that many of the interstellar molecules are observed to contain the rare isotopes as well as the common isotopes (*see also* Table 2). Such observations are of vital importance for several reasons.

1. They help to confirm the identity of molecules from their microwave spectra.
2. Comparison of the ratios of the rare to common isotopes in interstellar molecules compared to the solar system ratios provides an indicator of the nuclear history of the galaxy because certain isotopes can only be produced under specific conditions (e.g. Audouze, 1977; Guélin and Lequeux, 1980).
3. Since deuterium is considered to be primordial, then the existence of galactic gradients of this isotope, and indeed those of other elements, would be an indicator of nuclear burning (or processing) in the interiors of stars (Penzias, 1978, 1979; Wannier, 1980).
4. The D/H ratio is critical in cosmological models (Gott *et al.*, 1974).

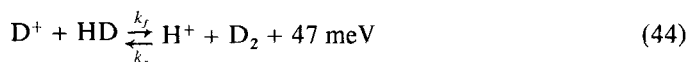
5. The isotopic content of certain molecules can, in principle, be used to obtain information on the physical conditions within interstellar clouds (we discuss this below).
6. The position of the rare isotope within the observed molecule (e.g. CH₃OD or CH₂DOH) can be an important clue to the chemistry leading to its production. For these reasons, much observational effort has been expended to detect molecules containing the rare isotopes and to determine their relative concentrations as a function of galactic coordinates, etc. (see for example Spitzer and Jenkins, 1975; Wannier *et al.*, 1976a,b; Townes, 1977; Penzias, 1979, 1980; Wannier, 1980).

Ideally, the relative isotopic abundances of each element should be determined for the cloud material as a whole, that is not only in the molecules, but also in the atoms and the dust grains. However, this obviously cannot be done and it has only been possible to determine the isotopic ratios within several specific molecules. Herein lies the big danger, since the process of isotope exchange in an ion-molecule encounter can preferentially 'fractionate' one of the isotopes into the molecule. In general, for small species it is found that the heavy isotope is fractionated into the more polyatomic species involved in the interaction, although this is not a golden rule (Adams *et al.*, 1981). Again, examples of this kind of reaction are (15) and (16). Discussions of isotope fractionation in interstellar clouds have been given by Watson (1976, 1977, 1980), Dalgarno and Black (1976) and Guélin and Lequeux (1980). We will discuss the interstellar importance of specific reactions and describe the appropriate laboratory studies beginning with those in which H/D exchange occurs.

HD is thought to be formed in diffuse clouds via reactions (15) and (16). The charge transfer reaction (15) has not been studied at thermal energies in the laboratory, but the rate coefficient for its endoergic direction (i.e. for H⁺ + D) has been calculated by Watson, Christensen and Deissler, (1978a). Note however, that reaction (16), which we re-write below as (43) for convenience, is also reversible and the ergicity of the reaction is simply obtained from a consideration of the zero-point energies of H₂ and HD and the recombination energies of H⁺ and D⁺. Thus:



i.e. the reaction is exoergic, having an enthalpy change, ΔH , of -40 meV for the production of HD from D⁺ and H₂ (termed the forward reaction with a rate coefficient k_f). The reverse rate coefficient is designated as k_r and at low temperatures (when $T \lesssim \Delta H/R$), $k_f > k_r$ and thus isotope fractionation can occur. The values of k_f (43) and k_r (44) for the analogous reaction:



have been measured by Fehsenfeld *et al.* (1973, 1974b) in a FA at 278 K, 200 K and 80 K. As expected $k_f(43) > k_r(44)$ and also $k_f(43)$ was only about a factor of two smaller than the gas kinetic value. Unfortunately, $k_r(43)$ and $k_f(44)$ cannot be studied satisfactorily in the FA because of competing forward and reverse reactions if HD is used as the ion source of reactant gas. However, the SIFT technique is ideally suited for the study of these forward and reverse reactions because the ion source gas is excluded from the flow tube (page 285) and so it has been possible to measure k_f and k_r for (43) and (44) at 200 K and 300 K (Henchman, Adams and Smith, 1981). From these measurements, it is a simple matter to determine the enthalpy and entropy change, ΔH and ΔS , in these reaction using the standard thermodynamic relations:

$$\Delta G = -RT \ln \left(\frac{k_f}{k_r} \right) = \Delta H - T\Delta S \quad (45)$$

i.e.

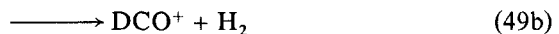
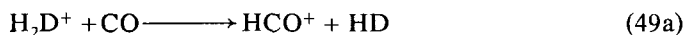
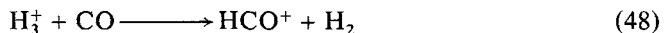
$$\ln \left(\frac{k_f}{k_r} \right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (46)$$

Thus ΔH and ΔS are obtained from an appropriate van't Hoff plot of $\ln(k_f/k_r)$ against $1/T$. The ΔH so obtained are in close agreement with the calculated values given above in (43) and (44) and the ΔS simply reflect the statistical factors involved. In fact, $\Delta S \sim +R \ln 2$ in (43) and $-R \ln 2$ in (44) as expected, and these data are a clear verification of the operation of statistical factors in these ion-molecule reactions. At 200 K, k_f (43) is, within error, equal to the gas kinetic value, $k_L (= 2.1 (-9) \text{ cm}^3 \text{ s}^{-1})$ and k_r (43) is much smaller with a value of $1 (-10) \text{ cm}^3 \text{ s}^{-1}$. However, for modelling interstellar ion-chemistry values of k_f and k_r are required at the much lower temperatures of interstellar gas clouds. Fortunately, these values can be obtained since for this reaction, and indeed for many other isotope exchange reactions, it is observed that at low temperatures (again where $T \lesssim \Delta H/R$) $k_f + k_r \rightarrow k_L$. Therefore, having determined ΔH and ΔS , then (k_f/k_r) can be obtained at any temperature, and by assuming that $k_f + k_r = k_L$, then both k_f and k_r can be obtained. By this means k_f (43) and k_r (43) have been determined at interstellar cloud temperatures and the implication of these data to interstellar HD formation has been discussed in a recent paper (Smith and Adams, 1981c). Thus, an extremely valuable guide to the rate coefficients for such isotope exchange reactions, obtained by inspection of SIFT data, is that at low temperatures $k_f + k_r \sim k_L$ and that in the low temperature limit, $k_f = k_L$.

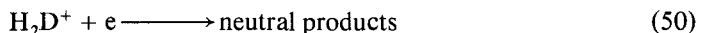
Another H/D exchange reaction which has received considerable attention is:



This is considered to be an important first stage in the deuteration of interstellar molecules, since it converts the H_3^+ ion (an important precursor in ion-chemical models, *see* Section 3 and Fig. 1) into H_2D^+ which can then react with other molecules and build D into the products. Thus a knowledge of k_f and k_r for (47) is vital. This reaction is also a critical stage in a model first proposed by Watson (1976, 1977) by which estimates can be obtained for the electron density, n_e , and the temperature, T , in dense interstellar clouds. In essence, the model is concerned with the formation and loss of H_2D^+ , HCO^+ and DCO^+ in interstellar clouds. Formation of the last two species is considered to be via the reactions:



H_2D^+ is formed in (47) and lost via the reverse of (47) and via (49). It is also lost by dissociative recombination with electrons (rate coefficient, α):

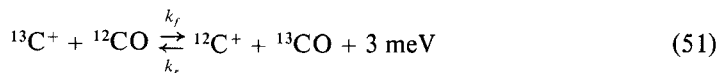


The rates of formation and loss of H_2D^+ are dependent on the rate coefficients k_f (47), k_r (47), k (49) and α (50). Reactions (48) and (49) involving CO are introduced since they generate the ions HCO^+ and DCO^+ which have both been detected in interstellar clouds, and this enables the $[\text{HCO}^+]/[\text{DCO}^+]$ concentration ratio to be related to the relative

concentrations of H_3^+ and H_2D^+ which so far have not been detected. A set of continuity equations describing the formation and loss of the ions involved in the model can be solved to relate the observed concentration ratio $[\text{HCO}^+]/[\text{DCO}^+]$ to n_e , T and the critical rate coefficients in the model, from which upper-limit values for n_e and T in the interstellar clouds can be obtained. The accuracy of the derived values of n_e and T will of course depend on the validity of the model and on the accuracy of the rate coefficients adopted. The first study of reaction (47) was made by Huntress and Anicich (1976) who measured $k_f(47)$ in an ICR cell to be $3 (-10) \text{ cm}^3 \text{ s}^{-1}$. To obtain $k_r(47)$ at gas cloud temperatures, Watson (1976) calculated ΔH for the reaction to be -15 meV and adopted the ICR value for $k_f(47)$ assuming it to be independent of temperature. These data have subsequently been used to estimate n_e and T in several clouds by other workers (Guélin *et al.*, 1977; Watson, Snyder and Hollis, 1978b; Turner and Zuckerman, 1978; Langer *et al.*, 1978; Wootten, Snell and Glassgold, 1979; Snell and Wootten, 1979).

Recent measurements in a SIFT (Adams and Smith, 1981a) of $k_f(47)$ and $k_r(47)$ over the temperature range 80 K to 295 K have shown that $k_f(47)$ at 295 K is $1.1 (-9) \text{ cm}^3 \text{ s}^{-1}$ (about a factor of four larger than the ICR value given above) increasing to $1.3 (-9) \text{ cm}^3 \text{ s}^{-1}$ at 80 K. The corresponding values for $k_r(47)$ are $5.6 (-10) \text{ cm}^3 \text{ s}^{-1}$ and $2.9 (-10) \text{ cm}^3 \text{ s}^{-1}$. So $k_f(47)$ increases and $k_r(47)$ decreases with decreasing temperature. The ΔH derived from a consideration of the temperature dependence of k_f/k_r (that is from a van't Hoff plot) is -8 meV , about a factor of two smaller than the calculated value of Watson. The involvement of statistical factors was also evident in the data; in this case $\Delta S \sim +R \ln 1.5$ as expected from the statistics of the reaction. The significance of these new data are that when they are used in the Watson model instead of the previous values they increase the upper limit estimate of n_e by a factor of six and lower the upper limit estimate of T by about a factor of 2 in interstellar clouds for any value of $[\text{HCO}^+]/[\text{DCO}^+]$. This is a very important result in the context of astrochemistry and astrophysics (for further discussion see Adams and Smith, 1981a). The SIFT data for (47) are also another indicator that the corresponding ICR data were obtained under suprathreshold conditions. They also indicate again the validity of the empirical rule that $k_f + k_r \sim k_L$ at low temperatures for these isotope exchange reactions. To consolidate this study, a detailed survey of the reactions of H_3^+ , H_2D^+ , D_2H^+ and D_3^+ with H_2 , HD and D_2 has been carried out (Smith and Adams, 1981b). This large body of data provides confirmation of the empirical rules for isotope exchange and provides further examples of the operation of statistical factors in these reactions.

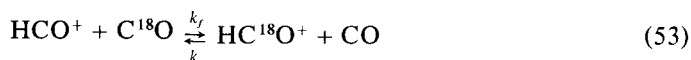
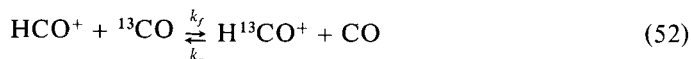
Isotope exchange involving heavier elements results in much smaller zero-point energy changes and so isotope fractionation of heavy elements will only become apparent at very low temperatures. It is therefore possible in interstellar clouds. To explain the larger $^{13}\text{C}/^{12}\text{C}$ ratio in interstellar CO relative to that in the solar system, Watson *et al.* (1976) suggested that fractionation of ^{13}C could occur in the reaction:



They measured $k_f(51)$ in an ICR to be $2 (-10) \text{ cm}^3 \text{ s}^{-1}$ and, assuming it to be temperature independent, they determined k_r at cloud temperatures using their calculated ergicity ($\Delta H = -3 \text{ meV}$). Using these data, Watson (1977, 1980) has considered in detail the fractionation of ^{13}C into CO in interstellar clouds and concludes that it can be significant if an appreciable fraction of the carbon in the cloud exists in the atomic form.

Recent SIFT studies of both $k_f(51)$ and $k_r(51)$ (Smith and Adams, 1980a) have shown that $k_f(51)$ increases with decreasing temperature reaching $7 (-10) \text{ cm}^3 \text{ s}^{-1}$ at 80 K, and that again $k_f + k_r \approx k_L$ ($\sim 1.2 (-9) \text{ cm}^3 \text{ s}^{-1}$ in this case) at the lowest temperatures. Thus at

cloud temperatures, $k_f(51)$ will be close to k_L , that is some six times greater than that assumed by Watson in his models. The van't Hoff plot constructed from the SIFT data provides a value for $\Delta H = -(3.5 \pm 0.4)$ meV, in good agreement with the calculated value. Smith and Adams (1980a) have considered the implications of the data to fractionation of ^{13}C in interstellar CO and conclude that the observed enrichment of ^{13}C in CO could be largely due to fractionation. However, the uncertainties in the ion-chemical model and the spread in the astronomical observations of isotope ratios are such that it cannot be ruled out that the $^{13}\text{C}/^{12}\text{C}$ ratio in the cloud material as a whole is somewhat greater than that in the solar system. This would, of course, in itself result in an apparent enrichment of ^{13}C in CO. In the same paper are reported the results of a similar study of isotope exchange in the reactions:

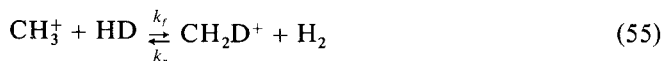


k_f is measurably different from k_r at 80 K for both (52) and (53) and will be increasingly so at lower temperatures. Therefore fractionation of both ^{13}C and ^{18}O can occur into HCO^+ via these reactions and, significantly, these heavy isotopes are seen to be enriched in interstellar HCO^+ . Only approximate values of ΔH could be obtained for (52) and (53) because of the small differences in k_f and k_r at 80 K. However the ΔH of ~ -1 meV is sufficient to explain the observed fractionation. The ΔH for the potentially important interstellar reaction (Guélin and Lequeux, 1980):



is similar to that for (52) and (53). The laboratory data relating to (54) and the interstellar implications of it are discussed in a recent paper (Adams and Smith, 1981c). Isotope exchange involving heavy elements has also been discussed by Langer *et al.* (1978, 1979).

Finally, we return again to H/D exchange. On pages 287 to 293 it was shown that CH_3^+ is an important precursor ion in the synthesis of larger molecules. Therefore it is important to note that CH_3^+ is rapidly deuterated in reaction with HD at low temperatures:



Again $k_f(55)$ reaches the limiting value, k_L , at low temperatures (Smith *et al.*, 1981c) $\Delta H = -28$ meV, and so CH_2D^+ will exist in interstellar clouds. It is therefore very probably an important precursor ion in the production of deuterated interstellar molecules. Clearly the density of CH_2D^+ relative to CH_3^+ depends on the equilibrium in (55) in the cloud environment.

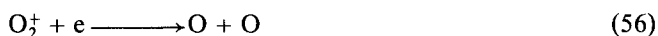
Many important interstellar ions such as HCO^+ , H_2CN^+ and NH_4^+ do not undergo H/D exchange in reaction with D_2 (and therefore presumably HD) at a measurable rate (*see* the data compilation by Huntress (1977)). This is to be expected for these reactions in the light of the collected SIFT data on isotope exchange reactions which indicate that the efficiency of isotope exchange in an ion-molecule encounter depends largely on the lifetime, τ_d , of the intermediate complex formed in the interaction. Thus, for example, in the $\text{H}_3\text{O}^+ + \text{D}_2\text{O}$ reaction, H/D exchange is very efficient (Smith *et al.*, 1980) at 300 K reflecting the strong bonding (and hence the long τ_d) in the $\text{H}_3\text{O}^+ \cdot \text{D}_2\text{O}$ complex. However for the $\text{CH}_3^+ + \text{CD}_4$ reaction in which a weakly bonded complex is involved H/D exchange is relatively inefficient at 300 K, but increases as the temperature reduces (*i.e.* as τ_d increases) (Adams *et al.*, 1981). τ_d can be estimated for these intermediate complexes by determining ternary

association rate coefficients (Smith and Adams, 1978a; Adams *et al.*, 1979) and these rate coefficients are extremely small for the association of HCO^+ , H_2CN^+ and NH_4^+ with H_2 (and presumably with HD and D_2). Therefore, the τ_d values are small and so isotope exchange in these reactions is expected to be very inefficient as is observed. This is useful guiding principle when considering isotope exchange reactions.

Neutralization processes

In the ion-chemical models described above, neutralization steps have to be invoked to convert positive ions to neutral molecules. Several ion neutralization processes are possible, such as positive ion-electron dissociative recombination, charge transfer with neutral species of low ionization energy, proton transfer to molecules of relatively large proton affinities and even neutralization on the surfaces of dust grains followed by desorption into the gas phase. If significant concentrations of negative ions are present in interstellar clouds then associative detachment and ion-ion mutual neutralization could become important.

Positive ion-electron dissociative recombination is a well known and much studied phenomenon in laboratory plasmas. It is exemplified by the reactions:



These three examples are chosen since they represent the varying degrees of certainty and doubt in the products of such reactions. Reaction (56) is perhaps the most studied dissociative recombination reaction of all. It has a rate coefficient, α , at 300 K of $2(-7) \text{ cm}^3 \text{ s}^{-1}$ which increases with decreasing temperature as $T^{-0.5}$. The products of the reaction are not in doubt and it is known that the product O atoms are electronically excited (Zipf, 1970). Reaction (57) involves a triatomic ion and, since polyatomic ions usually have larger α values (Biondi, 1973), it might have been thought that $\alpha(57) > \alpha(56)$. In fact at 300 K, $\alpha(56) \sim \alpha(57)$, which illustrates the dangers of generalization. The products of (57) are as indicated since they are simply dictated by the energetics of the reaction. Reaction (58) has also been studied in the laboratory (Huang, Biondi and Johnsen, 1976) and $\alpha = 1.5(-6) \text{ cm}^3 \text{ s}^{-1}$ at 300 K. However, the products are not known and, as indicated, several channels are energetically possible. However, the products for this reaction are not entirely a matter of speculation since Herbst (1978), using a statistical theory, has estimated the product distribution for (58) and for the dissociative recombination reactions of H_2CN^+ , H_3O^+ and CH_3^+ with electrons. For (58) he found that the three products indicated are about equally probable and that H-atom ejection is a significant channel in all four of the reactions considered. This gives some credence to the usual assumption made in interstellar ion-chemical models, that H-atom ejection is a likely result following the recombination of positive ions containing hydrogen.

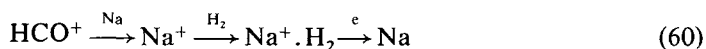
Several groups have contributed to the measurement of dissociative recombination coefficients using a variety of techniques. The greatest contribution has been made by Biondi and co-workers using a pulsed afterglow technique. The experimental and theoretical knowledge of this process up to 1970 has been reviewed by Bardsley and Biondi (1970). Since that time Biondi's group has added further data by determining α for several important interstellar ions, including H_3^+ and HCO^+ (Leu, Biondi and Johnsen, 1973a,b). They have also measured α for the cluster ion species, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_{0 \text{ to } 6}$ and $\text{NH}_4^+(\text{NH}_3)_{1,2}$ (Leu *et al.*, 1973c; Huang *et al.*, 1976) and find that α increases markedly with the number of ligands attached to the core ion, approaching the very large value of

$10^{-5} \text{ cm}^3 \text{ s}^{-1}$. Thus, α can vary between about $10^{-7} \text{ cm}^3 \text{ s}^{-1}$ and $10^{-5} \text{ cm}^3 \text{ s}^{-1}$ depending on the complexity of the ion involved (e.g. Biondi, 1973). Important laboratory studies have also been made by Dunn and co-workers using a low pressure ion trap technique to determine α values (Walls and Dunn, 1974; Heppner *et al.*, 1976) and by McGowan and co-workers (Auerbach *et al.*, 1977; Mitchell and McGowan, 1978; Mul and McGowan, 1979, 1980; McGowan *et al.*, 1979; Mul *et al.*, 1981) who have determined electron recombination cross sections for several likely interstellar ions using a merged beam technique. Calculated values of α for important interstellar ions are rare, but Giusti-Suzor and Lefebvre-Brion (1977) have calculated it for the $\text{CH}^+ + e$ reaction and arrive at a value much smaller than that measured by Mitchell and McGowan (1978). In view of the importance of this ion in diffuse cloud chemistry, it is important to resolve this discrepancy. Also, it has been suggested that the products of the electron recombination of H_2Cl^+ , which is formed in the reaction of HCl^+ and H_2 , will produce HCl in interstellar clouds. Since no HCl has been detected it seems probable that total dissociation of the H_2Cl^+ results (Smith and Adams, 1981a). Further experimental and theoretical work is badly needed in this area.

Charge transfer was suggested as a possible neutralization process in dense clouds by Oppenheimer and Dalgarno (1974). This becomes a viable process if significant concentrations of atoms with low ionization energies (e.g. Si, Ca, Na) exist in dense interstellar clouds. This, of course, would generate an atomic ion from a molecular ion, for example:



and since the process of radiative recombination, via which atomic ions are neutralized by electrons, is much less probable than dissociative recombination then a build-up of ionization in the clouds might be expected. However, there are two processes which might prevent this, one being that accretion of metal atoms onto dust grains would result in a small metal atom concentration in the gas phase (Duley and Millar, 1978), and the other that these atomic ions are known to associate rapidly with many molecules in ternary collisions (Spears and Ferguson, 1973) and therefore they could radiatively associate in dense clouds. This would result in molecular ions which could then rapidly recombine with electrons. However, if these free atoms do exist in sufficient concentrations then they could act as neutralization catalysts; e.g.



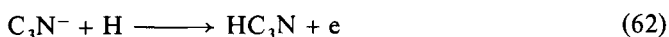
When proton transfer is energetically possible it is usually seen to occur rapidly (Bohme, 1975). Many of the interstellar molecules have large proton affinities and so it seems certain that this process will contribute to the production of some observed neutral molecules. For example, a sequence of reactions which seems highly probable is:



which generates CH_4 and HCO^+ , both observed interstellar species. Clearly proton transfer does not result in a net loss of ionization but nevertheless it does result in the neutralization of a particular ionic species.

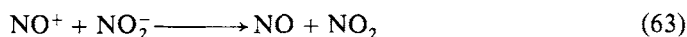
Since the early days of the subject, the possible involvement of negative ions in interstellar chemistry has been considered. McDowell (1961) suggested that the associative detachment reaction $\text{H}^- + \text{H} \rightarrow \text{H}_2 + e$ might be a gas phase route for H_2 production but this is now considered to be insufficiently rapid (Dalgarno and McCray, 1973). Recently,

Herbst (1981) has revived the negative ion discussion following the recent ICR observations of rapid binary (radiative) electron attachment to polyatomic fluorocarbons (Christodoulides and Christophorou, 1979; Woodin, Foster and Beauchamp, 1980). If this process occurs with reasonable efficiency between thermal electrons and the larger interstellar radicals, then a significant population of negative ions would exist and this could result in additional routes to the synthesis of larger molecules, for example via the process of associative detachment (Fehsenfeld, 1975a). An example of such a reaction might be:



in which the energy of the reaction is carried away by the free electron.

The process of mutual neutralization also could be invoked to generate neutral molecules e.g.:



This process has been studied in detail by Smith and co-workers (Smith and Church, 1976, 1977; Smith *et al.*, 1976, 1978a,b,c) and is known to be very fast at low temperatures although, in common with electron dissociative recombination, little is known about the products of any but the simplest reactions (Smith *et al.*, 1978b).

It is clear that there are many possible processes for the neutralization of interstellar ions and this is not a major problem in interstellar chemistry. However identifying the most important routes and the reaction products represents a major challenge especially in dense clouds.

5. CONCLUDING REMARKS

Active research into interstellar ion chemistry has been in progress for less than ten years yet, as we have tried to convey, considerable progress in understanding it has been achieved. The list of molecules observed in interstellar gas clouds has increased during this period to include more than fifty and with each new molecule discovered ion-chemical models have been updated and extended. These models indicate where additional laboratory data are required, and the efforts to acquire the data have led to the development of more appropriate experiments, especially those which can operate at suitably low temperatures. From these experiments, a better appreciation of ion chemistry at low temperatures is being obtained and this will accelerate the rate of understanding of interstellar chemistry. Thus, for example, it is now realized that the process of radiative association, originally thought to be significant only when the dominant neutral species H and H₂ are involved should now be considered to be a viable process for a much greater number of ion-neutral interactions. Also an understanding of isotope exchange in ion-molecule reactions is now being obtained and from this will follow an appreciation of the process of isotope fractionation and the extent of its involvement in the enrichment of rare isotopes in some interstellar molecules.

In this review, we have concentrated on the qualitative aspects of interstellar chemistry and have made only brief reference to detailed quantitative models. This is not meant to undervalue them. On the contrary, it is through these detailed models (which have so far only been constructed for diffuse clouds) that the greatest confidence is obtained in the validity of the basic interstellar chemistry outlined in this review. What are now needed are detailed astronomical observations of specific dense clouds in terms of molecules present, their relative densities and spatial distributions as a function of H₂ density, temperature, etc. (a challenging and time consuming process), followed by detailed quantitative models

of the specific clouds. This will undoubtedly stimulate more laboratory work to be carried out at appropriate temperatures and this should result in suggestions of other molecules to look for in the clouds. Much will then depend on spectroscopists to characterize molecular spectra and on the observers to increase detection sensitivities etc., all challenging and exciting problems.

Clearly many more molecules remain to be detected, presumably including many species of positive ions and perhaps some negative ions. The emissions from many of these are likely to be weak because of the expected low number densities. This is the technical challenge to radio astronomers. Meanwhile, many questions remain for the modellers and laboratory chemists and physicists to answer. For example, why are no chlorine-bearing molecules observed, have all the important routes to the polycyanoacetylenes been established, what are the important routes to the deuteration of the observed deuterated molecules, and is it likely that negative ions are significantly involved? The list is extensive. Much has been achieved and much more needs to be and will be achieved.

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