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Laboratory studies of isotope exchange in ion–neutral reactions: interstellar implications

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The rare stable isotopes of several elements (e.g. D, ^{13}C and ^{15}N) have been detected in several interstellar molecules, and their abundance relative to the more common isotope is often enhanced above that in the solar–terrestrial environment. Important questions to answer are to what extent the isotopic ratios in the molecules are representative of those in the cloud matter as a whole, and whether fractionation of the heavier isotope into the molecules via ion–molecule interactions is a significant process. A laboratory study of isotope exchange in ion–molecule reactions has therefore been carried out, the results of which indicate that fractionation of heavy isotopes can occur very efficiently at low temperatures. Consideration is given in this paper to reactions in which H–D, ^{12}C–^{13}C, ^{14}N–^{15}N and ^{16}O–^{18}O exchange occurs, and it is shown how better estimates of the electron density and the temperature in interstellar clouds have been obtained from these laboratory data.

1. INTRODUCTION

The rare stable isotopes of several elements (e.g. D, ^{13}C and ^{15}N) have been detected in several interstellar molecules (e.g. CO, HCO$^+$ and HCN) and the relative abundances of the common to the rare isotopes in some of these molecular species have been determined in dense clouds (see, for example, the reviews by Winnewisser *et al.* (1979) and Wannier (1980)). The data indicate that these relative abundances are often different from those expected on the basis of the terrestrial abundance ratios of the isotopes. For example, the terrestrial ratio ^{12}C/^{13}C is 89 yet the interstellar ratio as seen in CO and H$_2$CO is about half of this value (see, for example, Wannier *et al.* (1976) and Gardner & Whiteoak (1979); see also the reviews by Guélin & Lequeux (1980) and Penzias (1980)). Conversely, the ratio ^{14}N/^{15}N as seen in interstellar HCN is greater than the terrestrial ratio and is apparently smaller in the galactic disc than in the galactic centre (Linke *et al.* 1977). Isotope ratios in the galaxy are of vital importance for several reasons. They provide an indication of the nuclear history of the galaxy because certain isotopes can only be produced under specific conditions (see, for example, Audouze (1977) and Guélin & Lequeux (1980)). The H/D ratio is especially important since deuterium is considered to be largely primordial and thus the existence of galactic gradients in this isotope would be an indication of nuclear burning (or processing) within the interior of stars (Penzias 1978, 1979; Wannier 1980). In addition, the H/D ratio is a critical parameter in cosmological models (Gott *et al.* 1974). The isotope ratios of certain molecules can also be used to obtain information on the physical conditions within interstellar clouds (this is discussed in §3).

The molecules which have been observed in dense interstellar clouds via their millimetre wave emissions contain only a small mass fraction of the individual elements contained in the cloud matter and therefore the question arises as to what extent the isotope ratios in the observed molecules are representative of the cloud material as a whole. The answer to this question is not straightforward since there is the possibility that the heavier isotopes can be fractionated into the observed molecules by ion–molecule reactions (Dalgarno *et al.* 1973; Watson *et al.* 1976; Guélin *et al.* 1977; Langer *et al.* 1978). Isotope fractionation has been reviewed by Watson (1976, 1977, 1980), Dalgarno & Black (1976) and Guélin & Lequeux (1980). To illustrate this process, consider the reaction

$$D^+ + H_2 \underset{k_r}{\overset{k_f}{\rightleftarrows}} H^+ + HD. \tag{1}$$

Because of the difference in zero-point energy between H_2 and HD, reaction (1) is exoergic to the right and therefore at low temperature (T), differences will be observed between the forward and reverse rate coefficients, k_f and k_r respectively. The relative magnitude of these rate coefficients is described according to the thermodynamic relation, $\ln(k_f/k_r) = -\Delta G/RT = -\Delta H/RT + \Delta S/R$, where ΔG, ΔH and ΔS are the changes in free energy, enthalpy and entropy respectively. The value of ΔH (related to the ergicity, ΔE, of the reaction by $-\Delta H/R = \Delta E/k$) for molecular reactants is essentially given by the difference in zero-point energy between the reactants and the products, and the value of ΔS is given by the statistics of the isotope exchange. These parameters will be discussed below in relation to specific reactions. Isotope fractionation can therefore occur when k_f exceeds k_r and this process is expected to be significant at low temperatures where $T \lesssim -\Delta H/R$ and where entropy contributions ($T\Delta S$) to ΔG are small.

Thus before isotope ratios in the cloud material as a whole can be determined from the ratios observed in the molecules, the ion–chemical routes by which the particular observed molecules are produced, and the stages at which isotope fractionation can occur, must be determined. This is a very challenging problem for most of the complex molecules but not so difficult for small molecular species for which the gas-phase production reactions in interstellar clouds are better understood.

It was to provide critical experimental data for studies of ion–molecule reactions of interstellar significance that the selected ion flow tube (Sift) technique was developed. The technique is uniquely suited to the study of isotope exchange reactions at low temperatures. It is briefly described in the next section, and in subsequent sections the results of several studies of isotope exchange reactions thought to be critical in interstellar chemistry are described and their significance discussed.

2. Experimental

The selected ion flow tube (Sift) technique first developed by Adams & Smith (1976*a*, *b*) has been described in detail in a recent review (Smith & Adams 1979). Ions generated in a remote ion source are mass selected and injected into a flowing inert carrier gas (usually helium) and thermalized by collisions with carrier gas atoms while being convected down the flow tube. Reactant gases are introduced into the flow tube and both the loss rate of the primary ions with reactant gas addition and the nature of the product ions are determined by a downstream mass spectrometer–detection system. Hence the rate coefficients and product ion distributions can be determined for a wide variety of positive- or negative-ion–neutral atom or molecule reactions. The essential feature of the technique is that the reactant ion parent gas is excluded from the flow tube (unlike the similar flowing afterglow technique, which was developed by Ferguson *et al.* 1969), thus allowing isotope exchange reactions to be studied. Such studies are virtually impossible when the ion source gas and the reactant gas are both present in the flow tube because of complications resulting from simultaneous forward and reverse reactions. The temperature range available using the Sift is 80–600 K.

Since its inception the Sift has provided a considerable amount of data on several hundreds of ion–neutral reactions of fundamental, aeronomic and interstellar significance. Many of the data and their relevance to atmospheric and interstellar chemistry have been summarized in recent reviews (Smith & Adams 1978*a*, 1979, 1980*a*). The data of interstellar significance include the exoergic binary reactions of ions in the series, CH_n^+ (n = 0–4) (Smith & Adams 1977*a*, *b*, *c*, 1978*b*, *c*; Adams & Smith 1977, 1978), $C_2H_n^+$ (n = 0–4) (Adams & Smith 1977; Smith & Adams 1977*c*), H_nCO^+ (n = 0–3) (Adams *et al.* 1978), NH_n^+ (n = 0–4) (Adams *et al.* 1980; Smith & Adams 1981*a*) with many molecules and $C_2H_n^+$ with HCN (Mackay *et al.* 1980), the reactions of several ions with N and O atoms (Viggiano *et al.* 1980) and association reactions of CH_3^+ ions (Smith & Adams 1978*b*, *c*; Adams & Smith 1981*a*). Data on isotope exchange in ion–molecule reactions that have been obtained during the last year or so are summarized in the following section and their relevance to interstellar chemistry is discussed.

3. RESULTS OF THE STUDIES OF ISOTOPE EXCHANGE REACTIONS

Since isotope fractionation is a direct consequence of the differences in zero-point energy between isotopically labelled reactants and products, it is to be expected that this fractionation phenomenon will be most evident for hydrogen–deuterium exchange reactions. A recent study of the forward and reverse rate coefficients for reaction (1), i.e. $k_f(1)$ and $k_r(1)$, at 200 and 300 K and also the corresponding coefficients for the reaction

$$D^+ + HD \underset{k_r}{\overset{k_f}{\rightleftarrows}} H^+ + D_2 \qquad (2)$$

has verified that in each reaction $k_f > k_r$ and increasingly so at the lower temperature (Henchman *et al.* 1981). As mentioned in §1, ΔH and ΔS can be obtained for these reactions from k_f and k_r. Thus the $\Delta H/R$ obtained for reaction (1) is -464 K and for reaction (2) is -517 K, in good agreement with the values calculated on the basis of the different vibrational zero-point energies in the molecules and the different recombination energies of the ions (-462 and -541 K respectively). ΔH was calculated by assuming that the reactant and product molecules were also in their lowest rotational states. In the laboratory experiments the reactant H_2 and D_2 are in their 'normal' forms (that is the population distributions are o-H_2:p-H_2, 3:1; o-D_2:p-D_2, 2:1). However, it is easy to show that at the lowest temperature at which the experiments were carried out (200 K) the departures from the thermal rotational populations due to *ortho–para* constraints were not large enough to influence significantly the experimentally derived ΔH values; hence the good agreement between the experimentally determined and the calculated values of ΔH. In interstellar clouds the HD is expected to be almost entirely in the lowest rotational state (Dalgarno & Wright 1972). However, the rotational state distribution of the abundant H_2 is less certain, although it seems likely that the *ortho–para* distribution will be equilibrated in interstellar clouds (Dalgarno *et al.* 1973) which at the very low temperatures means that the H_2 will be largely in the lowest *para* state (i.e. J = 0). Under these circumstances the above calculation of ΔH for reaction (1) is appropriate and even if a significant fraction of the interstellar H_2 is in the lowest *ortho* state, which has an energy of 170.5 K above the lowest *para* state, there is expected to be little effect on $k_f(1)$, which will remain near to the gas kinetic limiting value (see below).

The ΔS values obtained for reaction (1) and (2) are *ca.* $R \ln 2$ and *ca.* $-R \ln 2$ respectively, and simply reflect the statistical factors involved in the reactions. Thus, for example probability of exchange in the $D^+ + H_2$ reaction is twice that for exchange in the $H^+ + HD$ reaction.

At 200 K, $k_f(1)$ is within error measured to be equal to the gas kinetic or collisional limiting value $k_L = 2.1 \times 10^{-9}$ cm³ s⁻¹ (Su & Bowers 1975), whereas $k_r(1)$ is much smaller, 1.1×10^{-10} cm³ s⁻¹, as is expected when $T < -\Delta H/R$. Reaction (1) is thought to be the major route to HD formation in interstellar clouds (Hartquist *et al.* 1978) and therefore it is important to know both $k_f(1)$ and $k_r(1)$ at gas cloud temperatures. Fortunately these coefficients can be determined at low temperautes from a knowledge of ΔH and ΔS for reaction (1) and from the apparently general result, obtained from Sift studies of several isotope exchange reactions, that $k_f + k_r = k_L$ at low temperatures (less than about 100 K). This result is substantiated by the data for reaction (1) and those for the other reactions discussed in this paper. Indeed, $k_f(1)$ is within error equal to k_L at 200 K and is therefore also expected to be so at interstellar cloud temperatures. The further interstellar implications of this new data have been discussed briefly in a recent letter (Smith & Adams 1981*b*). To reiterate, an extremely valuable guide to the rate coefficients for isotope exchange reactions, as obtained from Sift data, is that at low temperatures $k_f + k_r = k_L$ and therefore that k_f approaches k_L at $T \lesssim -\Delta H/R$.

H_3^+ is considered to be a most important ion in the synthesis of interstellar molecules and its reaction with HD, namely

$$H_3^+ + HD \underset{k_r}{\overset{k_f}{\rightleftarrows}} H_2D^+ + H_2, \qquad (3)$$

is especially important since it generates H_2D^+ and so reaction (3) is probably an important first stage in the production of deuterated molecules. Knowledge of $k_f(3)$ and $k_r(3)$ is vital if the relative concentration of H_2D^+ to H_3^+ in interstellar clouds is to be obtained. Reaction (3) is also a critical stage in a model first proposed by Watson (1976, 1977) by which upper limit estimates can be obtained for the electron density, $n_e/[H_2]$, 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

$$H_3^+ + CO \longrightarrow HCO^+ + H_2 \qquad (4)$$

and

$$H_2D^+ + CO \longrightarrow HCO^+ + HD \qquad (5a)$$

$$\longrightarrow DCO^+ + H_2. \qquad (5b)$$

H_2D^+ is formed in reaction (3) and lost by means of the reverse reaction (3) and by reaction (5). It is also lost by dissociative recombination with electrons (rate coefficient α):

$$H_2D^+ + e^- \longrightarrow \text{neutral products.} \qquad (6)$$

The rates of formation and loss of H_2D^+ are dependent on the rate coefficients $k_f(3)$, $k_r(3)$, $k(5)$ and $\alpha(6)$. Reactions (4) and (5) involving CO are introduced since they generate the ions HCO^+ and DCO^+, which have both been detected in interstellar clouds, and this enables the ratio $[HCO^+]/[DCO^+]$ 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 $[HCO^+]/[DCO^+]$ to $n_e/[H_2]$, T and the critical rate coefficients in the model, from which upper-limit values for $n_e/[H_2]$ and T in the interstellar clouds can be obtained. The accuracy of the derived values of $n_e/[H_2]$ 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 (3) was made by Huntress & Anicich (1976), who measured $k_f(3)$ in an ion cyclotron resonance (i.c.r.) cell to be 3×10^{-10} cm^3 s^{-1}. To obtain $k_r(3)$ at gas cloud temperatures, Watson (1976) calculated $\Delta H/R$ for this reaction, arriving at a value of -178 K and adopted the i.c.r value for $k_f(3)$ assuming it to be independent of temperature. These data have subsequently been used to estimate $n_e/[H_2]$ and T in several clouds by other workers (Guélin *et al.* 1977; Watson *et al.* 1978; Turner & Zuckerman 1978; Langer *et al.* 1978; Wootten *et al.* 1979; Snell & Wootten 1979).

Recent measurements in the Sift (Adams & Smith 1981 *b*) of $k_f(3)$ and $k_r(3)$ over the temperature range 80–295 K have shown that $k_f(3)$ at 295 K is 1.1×10^{-9} cm^3 s^{-1} (about four times larger than the i.c.r. value given above), increasing to 1.3×10^{-9} cm^3 s^{-1} at 80 K. The corresponding values of $k_r(3)$ are 5.6×10^{-10} cm^3 s^{-1} and 2.9×10^{-10} cm^3 s^{-1}, indicating again, as expected, that k_f increases and k_r decreases with decreasing temperature. The $\Delta H/R$ derived from these data is $-(90 \pm 10)$ K, i.e. about one half the value calculated by Watson (given above). However, a calculation of ΔH from the most recent values of the vibrational zero-point energies of H_3^+ and H_2D^+ (Carney 1980), ignoring rotational energy differences between the reactant and product molecules due to *ortho–para* configurations, gives a value of $\Delta H/R \approx -140$ K, significantly larger than the experimental value. The smaller ΔH determined experimentally is presumably partly because normal H_2 was used to determine $k_r(3)$. At 80 K the normal H_2 possesses an energy excess above equilibrium H_2 of about 40 K, comparable with the difference between the experimental and calculated values of ΔH. Some discrepancies can also arise because of departures from thermal equilibrium among the populations of the rotational states of the H_3^+ and H_2D^+ ions as a result of their *ortho–para* configurations. The magnitudes of such effects are difficult to assess. However, the proximity of the experimental and theoretically estimated ΔH suggests that the effect of differences in the rotational energies of the ions is small at 80 K. This may not be so under interstellar cloud conditions and the *ortho–para* configurations of the H_3^+ and H_2D^+ as well as the H_2 will have to be considered in estimating ΔH for reaction (3). Experiments are required, and indeed are planned, with the reactant H_2 varying from the pure *para*-H_2 to the 3 : 1 *ortho* : *para* normal H_2. Again, the involvement of statistical factors was evident in the data for reaction (3); in this case $\Delta S \approx R \ln 1.5$, as expected from the statistics of H_2D^+ and H_3^+ formation in the reactions. They also indicated again that $k_f + k_r = k_L$ and $k_f \rightarrow k_L$ at low temperatures for these isotope exchange reactions.

When these new data are used in the Watson model described above, they significantly change the upper limit estimates of $n_e/[H_2]$ and T in interstellar clouds from those obtained from the previous data. Because $k_f(3)$ is now expected to be equal to k_L ($= 1.7 \times 10^{-9}$ cm^3 s^{-1}) in cold interstellar clouds, that is some six times greater than that previously assumed, then $n_e/[H_2]$ is some six times greater than previous estimates for any given $[HCO^+]/[DCO^+]$ ratio. The new values of ΔH lead to estimates of T that are approximately one half the previous estimates if $\Delta H/R \approx -100$ K (appropriate to normal H_2) and somewhat more than one half if $\Delta H/R \approx -140$ K (appropriate to *para*-H_2). Thus for a ratio of $[HCO^+]/[DCO^+]$ in interstellar clouds of 100, then $n_e/[H_2] \lesssim 10^{-6}$ and $T \lesssim 15$ K. Further discussion of these results and their interstellar significance is given by Adams & Smith (1981 *b*).

A consequence of the smaller ΔH for reaction (3) is that $k_r(3)$ will be enhanced and therefore that the $[H_2D^+]/[H_3^+]$ density ratio in interstellar clouds will be reduced. So reaction (3) will be somewhat less important as a route for the deuteration of interstellar molecules than was previously thought. CH_3^+ is thought to be a most important ion in the synthesis of interstellar molecules, especially since it probably undergoes rapid radiative association reactions with many molecular species (Smith & Adams 1978*a*, *c*; Herbst 1976, 1980). Recently k_f and k_r for the reaction

$$CH_3^+ + HD \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CH_2D^+ + H_2 \qquad (7)$$

have between determined in a Sift (Smith & Adams, unpublished data), from which ΔH for the reaction has been estimated. These preliminary results indicate, in common with the other Sift data, that $k_f(7)$ reaches k_L ($= 1.33 \times 10^{-9}\ cm^3\ s^{-1}$) at low temperatures and that ΔH is large ($\Delta H/R \approx -300$ K). Thus in cold interstellar clouds the forward reaction will proceed with an efficiency of unity and the backward reaction will be totally unimportant. Therefore, once formed, the CH_2D^+ can undergo other reactions (including radiative association with H_2, producing CH_4D^+) and thus produce other deuterated molecules.

Isotope exchange involving heavy 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 therefore becomes possible in interstellar clouds. To explain the larger $^{13}C/^{12}C$ 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

$$^{13}C^+ + {}^{12}CO \underset{k_r}{\overset{k_f}{\rightleftharpoons}} {}^{12}C^+ + {}^{13}CO. \qquad (8)$$

They measured $k_f(8)$ in an i.c.r. to be $2 \times 10^{-10}\ cm^3\ s^{-1}$ and, assuming it to be temperature independent, they determined k_r at cloud temperatures using their calculated ergicity ($\Delta H/R = -35$ K). 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 $k_f(8)$ and $k_r(8)$ (Smith & Adams 1980*b*) have shown that $k_f(8)$ increases with decreasing temperature, reaching $7 \times 10^{-10}\ cm^3\ s^{-1}$ at 80 K, and that again $k_f + k_r = k_L$ ($\approx 1.2 \times 10^{-9}\ cm^3\ s^{-1}$ in this case) at the lowest temperatures. Thus at interstellar temperatures, $k_f(8)$ will be close to k_L, i.e. some six times greater than that assumed by Watson in his models. The data also provide a value for $\Delta H/R = -(40 \pm 5)$ K, in good agreement with the calculated value. Smith & Adams (1980*b*) 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 remains possible that the $^{13}C/^{12}C$ 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

$$HCO^+ + {}^{13}CO \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H^{13}CO^+ + CO \qquad (9)$$

and

$$HCO^+ + C^{18}O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} HC^{18}O^+ + CO; \qquad (10)$$

k_f is measurably different from k_r at 80 K for both reactions (9) and (10), 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$^+$ (Penzias 1980). Only approximate values of ΔH could be obtained for reactions (9) and (10) because of the small differences in k_f and k_r at 80 K. However, the $\Delta H/R$ of *ca.* -10 K is large enough to produce the observed fractionation. The ΔH for the potentially important interstellar reaction (Guélin & Lequeux 1980)

$$^{14}N_2H^+ + {}^{14}N^{15}N \rightleftharpoons {}^{14}N^{15}NH^+ + {}^{14}N_2 \tag{11}$$

is similar to that for reactions (9) and (10). Reaction (11) could thus lead to an enrichment of ^{15}N in N_2H^+, which would help in its detection. The laboratory data relating to reaction (11) and the interstellar implications of it are discussed in a recent paper (Adams & Smith 1981*c*). Isotope exchange involving heavy elements has also been discussed by Langer *et al.* (1978).

Conclusions

Exoergic isotope exchange in ion–molecule reactions can be very efficient at the low temperatures pertaining to interstellar clouds. The rate coefficients for such processes often approch the gas kinetic limiting value, k_L, at the lowest temperatures. The ergicities of these reactions are sufficiently large, especially for reactions involving H–D exchange, to result in fractionation of the heavier isotope into interstellar molecules, as is sometimes observed. In the light of the collected Sift data it is found that the efficiency of isotope exchange in ion–molecule encounters apparently depends on the lifetime against unimolecular decomposition, τ_d, of the intermediate complex formed in the encounter. τ_d is long, and isotope exchange is efficient, if the bonding of the ion–molecule pair that forms the complex is strong. This is so, for example, for the $H^+ \cdot H_2$ ($\equiv H_3^+$) and $CH_3^+ \cdot H_2$ ($\equiv CH_5^+$) complexes, and as has been indicated, isotope exchange is rapid in these systems at low temperatures. Conversely, the bonding in the complexes $HCO^+ \cdot H_2$ and $NH_4^+ \cdot H_2$, for example, is known to be very weak and, significantly, H–D exchange in the HCO$^+$ and NH_4^+ reactions with D_2 and HD is very inefficient (see the compilation by Huntress (1977) and Adams & Smith (1981*b*)). This is a useful guiding principle when considering isotope exchange in ion–molecule reactions.

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