INTERSTELLAR MOLECULE FORMATION;
RADIATIVE ASSOCIATION AND EXCHANGE REACTIONS

WILLIAM KLEMPERER

*Harvard University, Cambridge, Mass., U.S.A.*

1. Introduction

The present report is a summary of a study, made in collaboration with P. Solomon, on the formation of interstellar molecules by radiative association and chemical reactions. The model to be discussed is limited practically to gas phase reactions in an H$\textsc{i}$ region, where the principal constituents are atomic. It therefore is limited in scope and applicability. The role of the interstellar dust in this model is passive. It shields the region from radiation. Since a number of molecular species are dissociated by radiation and the extent of carbon ionization is determined by radiation, the radiation density is important in determining compositional equilibria.

In this work we estimate the rate coefficients of reactions of the type

$$A + B = AB + h\nu$$

and

$$AB + C = AC + B$$
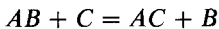
where A, B and C are atomic species, either neutral or ionic. The elements considered are H, O, C and N.

The kinetic temperature of the interstellar regions where molecular species exist is low. It is therefore necessary to consider only exothermic reactions. The dissociation energies of CH, CH$^+$, NH and OH are less than those of H$_2$, C$_2$, C$_2^+$, O$_2$, and N$_2$ [1]. This has two consequences. First, with respect to H$_2$, it cannot be a source of CH and CH$^+$ from the above type of reaction nor as shall be shown can it be produced in appreciable quantity by the reactions $CH + H = C + H_2$ or $CH^+ + H = C^+ + H_2$. Thus the question of the abundance of H$_2$ will not enter except in altering the atomic abundance ratios. Secondly the species CH and CH$^+$ cannot be formed by an elementary atom molecule exchange reaction such as $C_2 + H = CH + C$.

A summary of reactions and their rate coefficients are listed in Table I. As may be seen from this table, there are a large number of reactions determining compositional and ionization equilibria in this model. Not listed in this table are photo-ionization cross-sections or electron ion recombination rates which are fairly standard. We briefly discuss the values of these rate coefficients here. These are discussed in detail in the article with Solomon.

2. Radiative Association

Of the hydrides only CH and CH$^+$ can be formed by electric dipole allowed, exothermic, radiative association. The process has been discussed for both CH and CH$^+$

TABLE I

Important reactions and their rate constants

Reaction	Rate constant cc/particle sec^{-1}
A Radiative association	
$C^+ + H = CH^+ + h\nu$	$7 \times 10^{-17}\ T < 50°$
	$2 \times 10^{-17}\ T \approx 200$
$C + H = CH + h\nu$	$(3.0 - (T - 20) \cdot 0.06) \times 10^{-17}$
	$10 \leqslant T \leqslant 30$
	$3 \times 10^{-18}\ T \approx 100$
B Ion molecule	
$CH^+ + O = CO + H^+$	
$CH^+ + O = CO^+ + H$	1×10^{-9}
$CO^+ + H = CO + H^+$	
$CH^+ + N = CN + H^+$	1×10^{-9}
$CH^+ + C = C_2^+ + H$	1×10^{-9}
$CH + C^+ = C_2^+ + H$	1×10^{-9}
$CH^+ + H = C^+ + H_2$	$7.5 \times 10^{-15}\ T^{5/4}$
$C_2^+ + O = CO + C^+$	1×10^{-9}
$C_2^+ + N = CN + C^+$	1×10^{-9}
C Charge exchange	
$CO^+ + H = CO + H^+$	10^{-9}
$CN^+ + H = CN + H^+$	10^{-9}
$Na + C^+ = Na^+ + C$	2×10^{-9}
$K + C^+ = K^+ + C$	2×10^{-9}
$Ca + C^+ = Ca^+ + C$	2×10^{-9}
D Neutral–neutral	
$CH + O = CO + H$	4×10^{-11}
$CH + C = C_2 + H$	4×10^{-11}
$CH + N = CN + H$	4×10^{-11}
$C_2 + O = CO + C$	3×10^{-11}
$C_2 + N = CN + C$	3×10^{-11}
$CN + O = CO + N$	$10^{-11}\ e^{-1200/T}$
$CN + N = C + N_2$	10^{-13}
$CH + H = C + H_2$	10^{-14}

E Photo dissociation transitions		Photo dissociation rate
λÅ	f	$u = 34 \times 10^{-18}$ ergs/Å $\lambda > 912$
CH 3000	3×10^{-3}	sec^{-1}
2500	3×10^{-4}	
1500	2×10^{-3}	$5 \times 10^{-11}\ e^{-0.55\tau_{1000}}$
1200	3×10^{-2}	
CH$^+$ 950	1×10^{-2}	$3 \times 10^{-12}\ e^{-\tau_{1000}}$
CN 1200	5×10^{-2}	$4 \times 10^{-11}\ e^{-0.83\tau_{1000}}$
CO 1050	4×10^{-3}	
$\sigma = 1 \times 10^{-17}\ \lambda < 960$		$2 \times 10^{-11}\ e^{-1.1\tau_{1000}}$
$\left. \begin{matrix} C_2 \\ C_2^+ \end{matrix} \right\}$ 1200 10^{-2}		$8 \times 10^{-12}\ e^{-0.83\tau_{1000}}$

F Miscellaneous reactions	
$CH^+ + e = CH + h\nu$	$5.7 \times 10^{-9}\ T^{-0.7}$
$CH^+ + e = C + H$	$5.7 \times 10^{-9}\ T^{-0.7}$
$CH + h\nu = CH^+ + e$	$1.8 \times 10^{-10}\ e^{-0.95\tau_{1000}}$
$f = 5 \times 10^{-2}\ \lambda = 1130$	
$\sigma = 1.1 \times 10^{-18}\ \lambda < 1165$	
$H + \gamma = H^+ + e$	1×10^{-15}

previously [2]. The rate constants given here are greater than previous estimates for the following reasons. For the reaction $C^+ + H = CH^+ + h\nu$ the rate coefficient is the product of the collision number times the probability of $A\,^1\Pi \to X\,^1\Sigma$ emission during the life of the collision complex. (We do not consider emission in the triplet system, but regard this point as unanswered. The possibility of triplet emission will increase the rate of radiative association above that estimated here.) At low temperatures two effects must be considered which have previously been ignored. The collision number is increased, because of the finite wavelength of the hydrogen atom, over the classical collision number. The probability of $^1\Pi \to {}^1\Sigma$ emission is increased over that expected

TABLE II

Simplified orbital model of oscillator strengths of CH and CH$^+$ transitions

	$3\sigma^2 1\pi$	$3\sigma 1\pi^2$	Ratio of line strengths	f_{obs}	f_{calc}
CH	$X\,^2\Pi \to$	$A\,^2\Delta$	1	5.2×10^{-3}	5.6×10^{-3}
	$X\,^2\Pi \to$	$B\,^2\Sigma^-$	$\tfrac{3}{4}$	2.8×10^{-3}	4.6×10^{-3}
	$X\,^2\Pi \to$	$C\,^2\Sigma^+$	$\tfrac{1}{2}$	5.6×10^{-3}	3.9×10^{-3}
	$3\sigma^2$	$3\sigma 1\pi$			
CH$^+$	$X\,^1\Sigma^+ \to$	$A\,^1\Pi$	2		2.2×10^{-2}

for a single traversal of the $^1\Pi$ potential curve by the inability of the system (CH$^+$) to separate into the upper $(P_{3/2})$ fine structure component of C$^+$. The dipole strength of the stabilizing transition is obtained from the estimate that the absorption oscillator strength of the $^1\Sigma \to {}^1\Pi$ transition is $f = 2.2 \times 10^{-2}$. The arguments for this oscillator strength are given in Table II. We assume that the molecular orbitals of the active electron are the same in CH and CH$^+$ for the ground and first excited configuration.

Identical arguments for the system $C + H = CH + h\nu$, with regard to fine structure statistical trapping and an increase over classical collision number leads to the increase of rate constant over previous estimates.

3. Ion–Neutral

The interaction potential is

$$V = - e^2 \alpha_N / 2r^4$$

where e is the charge of the electron, α_N the polarizability of the neutral and r the internuclear distance. We have assumed that exothermic reactions occur on every classical collision leading to capture unless there is specific laboratory data to the contrary. The entries in Table I show for which reactions this occurs. These cases are discussed in the article with Solomon.

4. Neutral–Neutral

The classical collision number is taken for the rate of exothermic reactions unless specific laboratory data exists to the contrary.

5. Charge Exchange

For exothermic reactions such as $Na + C^+ = Na^+ + C$ the rate is taken to be one half the classical collision frequency. The large number of atomic carbon electronic states for which this reaction remains exothermic leads to the expectation that molecular potential energy curve crossing will occur frequently. Figure 1 shows the atomic energy level scheme for $Na + C^+ = Na^+ + C$. The symmetry of the molecular states are shown. There are no calculations of molecular potential energy curves for this system. Thus it is not possible to give the details of the curve crossing. It appears
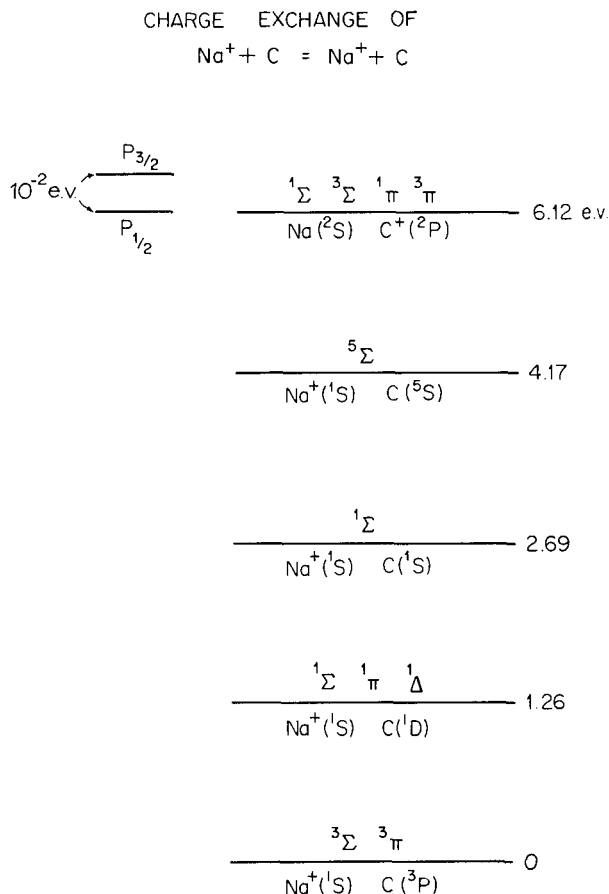

Fig. 1.

reasonable to assume that the $^1\Sigma$ state produced from $C(^1S)+Na^+$ will be repelled by the lower $^1\Sigma$ state. The repelled state will then intersect $^1\Sigma$ generated from $C^+(^2P)$ $+Na(^2S)$. We note that since interstellar C^+ is in the $P_{1/2}$ fine structure component that in low energy collisions the system cannot separate into the $P_{3/2}$ state. Thus for the $^1\Sigma$ intersection it is expected that nearly $\frac{3}{12}=\frac{1}{4}$ of the classical collisions lead to charge exchange. It is expected that there are some contributions to charge exchange from molecular curves of other symmetry. We assume therefore that one half of all classical collisions lead to charge exchange. In the calculation of Na/Na^+ equilibria it is assumed that reactions such as $Si^++Na=Na^++Si$ will occur with the rate constant given for C^++Na.

6. Photo-Dissociation

The photo-dissociation rates are listed together with the photo-dissociating transitions. The rates are calculated for a radiation field of 34×10^{-18} erg/Å. The interstellar dust is assumed to shield the region as $\exp(-\tau_{1000}/\lambda)$. The photo-dissociation rates are expressed for tabular convenience as

$$k = k_0 \exp(-a\tau_{1000})$$

where a is a fitting parameter for each reaction. In actual numerical calculations we have used the calculated rates rather than the fitted ones. The arguments for the
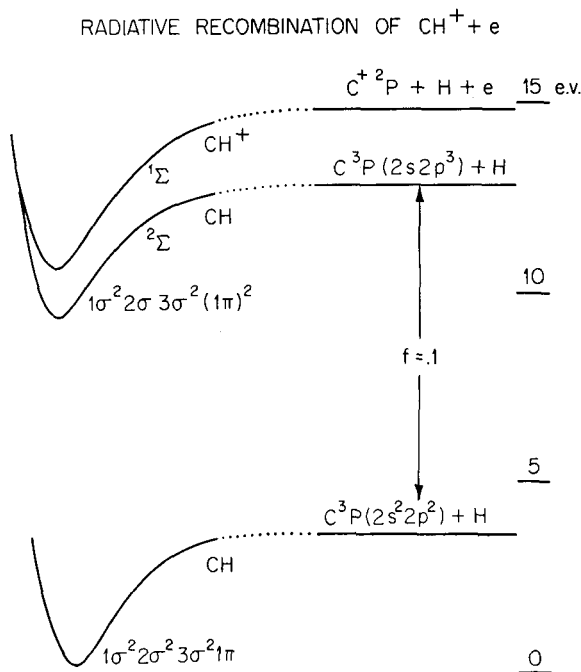

Fig. 2.

values chosen for the strengths and wavelengths of photo-dissociating transitions are given in the article with Solomon.

7. Miscellaneous Reactions

Electron production occurs by carbon and metal photo-ionization and cosmic ray ionization of atomic hydrogen. The photo-ionization cross sections used are standard and not listed. The radiative association reaction

$$CH^+ + e = CH + h\nu$$
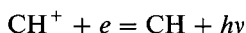
is assumed to proceed primarily by dielectronic recombination [3] (inverse autoionization). The relevant potential energy curves are shown in Figure 2. The oscillator strength for the shown upper bound $^2\Sigma$ CH state to the set of lower CH bound states is assumed to be close to that for the corresponding atomic transition, namely $f = 0.1$. The rate constant for recombination is taken to be 30 times that of proton recombination. We include dissociative recombination and assume the rate constant is the same as that for radiative recombination.

TABLE III

CH Equilibrium

Process	Rate constant (atom/cm^3 sec^{-1})	Rate $T = 20° \; n_H = 50/cm^3$ $\tau_{1000} = 2$
$C + H = CH + h\nu$	$(3 - 0.06(T - 20)) \times 10^{-17}$	2.3×10^{-18}
$CH^+ + e = CH + h\nu$	$5.7 \times 10^{-9} \; T^{-0.7}$	1.3×10^{-17}
$CH + C^+ = C_2^+ + H$	$1 \quad \times 10^{-9}$	1.4×10^{-11}
$\qquad O \quad CO$		
$CH + N = CN + H$	$4 \quad \times 10^{-11}$	1.5×10^{-12}
$\qquad C = C_2$		
$CH + H = C + H_2$	10^{-14} or less	$5 \quad \times 10^{-13}$
$CH + h\nu = C + H$	$5 \quad \times 10^{-11} \; e^{-0.55 \, \tau_{1000}}$	1.7×10^{-11}
$CH + h\nu = CH^+ + e$	$1.8 \times 10^{-10} \; e^{-0.95 \, \tau_{1000}}$	2.7×10^{-11}

TABLE IV

Na/Na$^+$ Equilibrium

Process	Rate constant	Rate $T = 20° \; n_H = 50/cm^3$ $\tau_{1000} = 2$
$Na^+ + e = Na + h\nu$	$1.5 \times 10^{-10} \; T^{-0.7}$	1.1×10^{-16}
$Na + h\nu = Na^+ + e$	$7.5 \times 10^{-12} \; e^{-0.67 \, \tau_{1000}}$	$2 \quad \times 10^{-12}$
$Na + C^+ = Na^+ + C$	$2 \quad \times 10^{-9}$	5.4×10^{-11}

8. Results

In using the rate coefficients of Table I we assume that the composition of the region is primarily atomic. The electron density and all atomic ionization equilibria are calculated ignoring molecules. The atomic abundance ratios are taken from Allen [4]. The three parameters are temperature, density and shielding. The value of τ_{1000} is taken to be $2A_v$. Thus only density and temperature are then free parameters.

Tables III and IV show the processes involved in the equilibria of two species namely CH and Na. The rates of the reactions are given for the conditions density $= 50/\text{cm}^3$, $T = 20°$, $\tau_{1000} = 2$. There are a relatively large number of reactions which

TABLE V
Interstellar abundances zeta Ophiuchi

Herbig observation		Calculation
		$T = 20°$, $n_H = 50/\text{cc}$
		$N_H = 1.5 \times 10^{21}/\text{cm}^2$
		$\tau_{1000} = 2$
	Column number atom/cm²	
CH	4.3×10^{13}	$9 \ \times 10^{12}$
CH$^+$	2.6×10^{13} ($f_{el} = 2.2 \times 10^{-2}$)	9.1×10^{12}
CN	8.3×10^{12}	7.8×10^{12}
Na	4.9×10^{13}	4.4×10^{13}
Ca^I/Ca^{II}	10^{-2}	1.9×10^{-2}
NH	$<7 \ \times 10^{12}$	0
OH	$<8 \ \times 10^{13}$	0
CO$^+$	$<3.5 \times 10^{13}$	$<6 \ \times 10^9$
CO	–	1.1×10^{14}
C$_2^+$ + C$_2$	–	$3 \ \times 10^{12}$
(e)	–	$0.06/\text{cc}$
C^I/C^{II}		0.11

are important in CH equilibria. As conditions change the relative importance of different reactions change thus giving some stability to the abundance of CH. In Na/Na$^+$ equilibria we note that the charge exchange reaction is much more important than photo-ionization. This implies that roughly the density of neutral Na varies approximately as the inverse square root of the density, a not altogether obvious result.

The comparison of the present theory with observation is severely hampered by a lack of quantitative observational data. The model study by Herbig [5] of ζ OPH provides by far the best example for comparison. Table V shows the comparison of model and observation. The column number of hydrogen and the optical shielding are fixed from observation. The temperature and density are assumed. Relatively good quantitative agreement is obtained. Of perhaps even greater significance is the qualitative agreement.

References

[1] Wilkinson, P. G.: 1963, *Astrophys. J.* **138**, 778.
[2] Bates, D. R.: 1951, *Monthly Notices Roy. Astron. Soc.* **111**, 303; Bates, D. R. and Spitzer, L.: 2951, *Astrophys. J.* **113**, 441.
[3] Autoionization 1966 (ed. by A. Temkin), Mono Book Corp., Baltimore.
[4] Allen, C. W.: 1963, *Astrophysical Quantities*, 2nd ed., London.
[5] Herbig, G. H.: 1968, *Z. Astrophysik* **68**, 243.