STOCHASTIC THEORY OF MOLECULE FORMATION ON DUST

S. B. CHARNLEY

Space Science Division, NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035 Received 2001 June 6; accepted 2001 October 3; published 2001 November 1

ABSTRACT

The formation of interstellar molecules on the surfaces of dust grains is calculated in the framework of stochastic reaction kinetics. The master equation and the state transition probabilities are defined, and the growth of grain mantles following accretion and reaction of gas-phase species is computed. The results are compared to the observed composition and structure of interstellar ices. The differences between this approach to gas-grain kinetics and previous work is discussed, and possible extensions of the theory are outlined.

Subject headings: dust, extinction — ISM: molecules — methods: numerical — methods: statistical

1. INTRODUCTION

The discrete, random nature of the accretion and reaction of gas-phase atoms and molecules on interstellar dust grains means that accurate theoretical models of grain mantle growth necessarily involve a fully stochastic formulation of the problem involving a solution of the associated master equation (Charnley 1998, hereafter Paper I). A stochastic treatment of gas-phase chemical evolution of dense interstellar clouds has already been given (Paper I). The aim of this Letter is to describe the extension of the stochastic approach to reaction kinetics on interstellar grains and demonstrate the simulation algorithm.

2. STOCHASTIC SURFACE KINETICS

The use of simple (univariate and bivariate) master equations is common in surface science (e.g., Montroll 1980). The stochastic treatment of multivariate grain surface reactions can be formulated and solved in the same way as described in Paper I. There are, however, important conceptual differences. Only the surface monolayer, in contact with the gas, is to be considered; the number of particles available for chemical reactions is limited to the maximum number that can be accommodated in this monolayer. Simple estimates indicate that an idealized, spherical, refractory grain core will contain $\mathcal{N} = 10^6$ binding sites (e.g., Tielens & Allamandola 1987), and it will be assumed that this is fixed for all subsequent monolayers. Interstellar ice mantles contain many monolayers with differing composition with depth into the mantle; this structure must also be accounted for when formulating the kinetic problem.

We denote X_i as the number of particles of type *i* in the *surface monolayer* and X_i^b as the total number within the *bulk* mantle (i.e., all monolayers). The chemical state of the surface is determined by the population vector $\mathbf{x} = \{X_i\}$, and this can change through the occurrence of one, μ , say, of the *M* possible surface processes: accretion from the gas, surface desorption, or chemical reaction. The probability that the surface is in state $\{X_i\}$ at time *t* is $P(\mathbf{x}; t)$, and this evolves according to the master equation

$$\frac{\partial}{\partial t}P(\boldsymbol{x}; t) = \sum_{\mu}^{M} [W_{\mu}(\boldsymbol{x} - \boldsymbol{s}_{\mu})P(\boldsymbol{x} - \boldsymbol{s}_{\mu}; t) - W_{\mu}(\boldsymbol{x})P(\boldsymbol{x}; t)],$$
(1)

where the probability per unit time of the surface making a

state transition in the infinitesimal time interval [t, t + dt], by virtue of process μ occurring, given that it is in state \mathbf{x} at time t, is $W_{\mu}(\mathbf{x})$. The integer vector s_{μ} accounts for the stoichiometry of reaction μ . For a prescribed set of M surface processes and suitably defined transition rates, $W_{\mu}(\mathbf{x})$, the master equation can be simulated to obtain the mean and variance of the surface populations and the overall bulk mantle composition as functions of time. For bimolecular surface reactions, it is convenient to write $W_{\mu}(\mathbf{x})$ in the form

$$W_{\mu}(\mathbf{x})dt = \gamma_{\mu}q_{\mu}(\mathbf{x})p_{\mu}\,dt, \quad \mu = 1, 2, \dots, M, \qquad (2)$$

where γ_{μ} (s⁻¹) is a stochastic reaction rate constant for surface processes, analogous to c_{μ} for gas-phase reactions (Paper I), and $q_{\mu}(\mathbf{x})$ is a probability involving a combinatorial evaluation of the number of distinct ways surface process μ can occur. The probability factor p_{μ} allows the incorporation of reactions with activation energy barriers. For example, for quantum mechanical tunneling through a square potential barrier of height E_{μ} and width L, $p_{\mu} = \exp \left[-2L \left(2m_{\rm H}E_{\mu}\right)^{1/2}/\hbar\right]$; for no barrier, $p_{\mu} = 1$.

What distinguishes the stochastic approach is that the particle populations play a fundamental role in determining the reaction probabilities. For example, if at any instant $X_j = 0$, the reaction i + j cannot occur if a particle *i* migrates to an adjacent site—only processes that change the chemical state of the surface are relevant. For each surface process, the underlying physics and characteristic timescale, τ_{μ} , are well known (e.g., Tielens & Allamandola 1987), and taking $\gamma_{\mu} = \tau_{\mu}^{-1}$, the $W_{\mu}(\mathbf{x})$ are defined as follows.

2.1. Gas-Grain Interaction

We consider a reaction volume V containing the gas particles and the surface of one dust grain. Each species *i* has gas-phase population of Y_i and can interact with the grain surface population through accretion and desorption.

2.1.1. Accretion

For typical interstellar dust parameters and unit sticking at 10 K, particles of species *i* are lost from the gas by accretion on the grain at a rate of $10^{-5}M_i^{-0.5}Y_iV^{-1}$ (s⁻¹), where M_i is the molecular weight (e.g., Charnley 1997). This is also the rate at which they arrive at the grain surface. From the perspective of the gas and the grain chemistries, an accretion event can be viewed, respectively, as the spontaneous chemical annihilation

and creation of particles. Overall, accretion changes the populations by $Y_i \rightarrow Y_i - 1$ and $X_i \rightarrow X_i + 1$. As species *i* can accrete in Y_i distinct ways, one has

$$W_{\mu}(\mathbf{x})dt = 10^{-5}M_i^{-0.5}Y_iV^{-1} dt.$$
(3)

2.1.2. Desorption

Atoms and molecules can be desorbed from sites on the surface monolayer by a number of processes (e.g., Willacy & Millar 1998). Desorption, occurring at some rate ξ_i , can be regarded as the inverse process to accretion. For the case of thermal desorption, the probability of a particle *i* being lost from the surface monolayer in the infinitesimal time interval [t, t + dt] is

$$W_{\mu}(\mathbf{x})dt = \nu \exp\left(-\frac{E_B}{kT_d}\right) X_i dt, \qquad (4)$$

where ν is the vibrational frequency of the particle in a surface binding site (~10¹² s⁻¹), T_d is the surface temperature, and E_B is the binding energy for physisorption.

2.2. Surface Reactions

At 10 K, only atoms will be mobile on grain surfaces. Unlike previous formulations of this problem, the timescale over which the surface state changes through chemical reactions is that of the one-step process of a migrating atom moving to an adjacent site, not the timescale to explore the entire grain surface (Charnley 2001).

Hydrogen atoms migrate by quantum mechanical tunneling on a characteristic timescale of $\tau_{\rm H} \sim 10^{-12}$ s (Hollenbach & Salpeter 1970; Tielens & Allamandola 1987). Heavy atoms (O, C, N) move by thermal hopping, and the timescale for this is $\tau_{\rm hop}$. Atomic migration by these processes leads to reactions among the atoms and also with other, relatively static, surface radicals and closed-shell molecules. Hence, for H atom reactions, one has

$$W_{\mu}(\mathbf{x})dt = \gamma_{\rm H} q_{\mu}(\mathbf{x}) p_{\mu} dt, \qquad (5)$$

where $\gamma_{\rm H} = \tau_{\rm H}^{-1}$. For reactions involving migration by hopping, one has

$$W_{\mu}(\boldsymbol{x})dt = \gamma_{\rm hop}q_{\mu}(\boldsymbol{x})p_{\mu}\,dt,\tag{6}$$

where

$$\gamma_{\rm hop} = \nu \exp\left(-\frac{E_D}{kT_d}\right). \tag{7}$$

Here E_D is the energy barrier for surface diffusion, typically $E_D \approx (0.3-0.5)E_B \approx 240$ K (Tielens & Allamandola 1987; Caselli, Hasegawa, & Herbst 1998). For μ being the reaction between *i* and *j*, $q_{\mu}(\mathbf{x})$ is given by a hypergeometric distribution (e.g., Feller 1950):

$$q_{\mu}(\mathbf{x}) = \frac{(X_i 1) (X_j 1)}{(N2)} = \frac{X_i X_j}{\mathcal{N}(\mathcal{N} - 1)}.$$
 (8)

This expression assumes that the particles are randomly distributed on the surface. More sophisticated treatments are the "quasi-chemical" approximation or a full lattice-gas simulation of the surface kinetics (Zhdanov 1981; Chopard et al. 1993; Lukkien et al. 1998). Given our ignorance of important surface quantities, the mean field approximation is sufficient to illustrate the stochastic approach to surface kinetics. Equation (8) also assumes that when a tunneling or hopping event occurs on the surface involving an atom i, $W_{\mu}(\mathbf{x})$ is proportional to the total number of j particles currently present. This tends to overestimate $q_{\mu}(\mathbf{x})$ when the population X_j is small. Physically, transitions are only to nearest neighbor sites, of which there are m, say, and it is the distribution of j particles in these sites that determines $q_{\mu}(\mathbf{x})$. A more refined expression for $q_{\mu}(\mathbf{x})$ involving m could be obtained by solving a slightly more involved combinatorial problem.

The constraint that only \mathcal{N} particles can take part in the surface chemistry, and the fact that the mantles grow one particle at a time, have to be both accounted for in the simulation. After the first monolayer forms, these molecules are subsequently covered by accreting species as the next monolayer forms. Hence, the reactive surface population changes as particles are buried and removed. Covered particles can also be returned to the surface population by chemical reactions or desorption. These processes can be accounted for by periodically recomputing and storing the population of the subsurface monolayer, $X_i^s(t)$. The following strategy was adopted. When an atom or a molecule arrives on the surface, a molecule is randomly removed from the surface population $\{X_i\}$. When the covering is by a heavy atom such as oxygen, at the next selected oxidation reaction, a molecule in $\{X_i^s\}$ is selected at random and returned to the surface. When the covering is by a hydrogen atom, the type of molecule covered is noted and one of these is returned to the surface after the next H atom reaction selected. When the selected reaction is H_2 formation, two particles are uncovered. It is necessary to use $\{X_i^s\}$ rather than the bulk mantle population $\{X_i^b\}$. Otherwise, when H₂ formation comes to dominate the kinetics, as it does at later times in the simulations presented here, the surface would rapidly become unphysically dominated by H₂O; at this time, most of the H₂O molecules present actually lie many monolayers below the surface.

3. STOCHASTIC SIMULATION

We consider a simple reaction system involving the arrival of H, O, and CO molecules from the gas, no desorption, and the exothermic surface reactions: $H + H \rightarrow H_2$, $O + O \rightarrow O_2$, $O + H \rightarrow OH$, and $OH + H \rightarrow H_2O$. We also consider the oxidation of CO and assume that the reaction

$$\mathbf{O} + \mathbf{CO} \to \mathbf{CO}_2 \tag{9}$$

proceeds with no activation energy barrier. Due to the uncertainty surrounding the nonthermal processes that contribute to desorption in cold clouds, we ignore desorption in this first study. This simple surface model has been used previously to compare the steady state results of Monte Carlo simulations with those of other approaches (e.g., Tielens & Charnley 1997; Caselli et al. 1998) and includes the most important reactions understood to occur on grains. There is a lower limit on the number of particles in a gas-grain simulation. This depends on the fact that one must be able to resolve one grain for a given gas-dust number density ratio and, less strongly, on the number of possible monolayers to be considered. For $n(H_2) = 10^4$ cm⁻³, we assume a reaction volume of $V = 10^7$ cm³. Initially, the gas-phase populations are $Y_i = f_i n(H_2)V$, where f_i is the fractional abundance of *i*. A fixed CHARNLEY





105

10⁶

104

 10^{-3}

1000

value of $Y_{\rm H} = 10^7$ was used in all models, corresponding to $n({\rm H}) = 1 {\rm ~cm^{-3}}$. Simulations were performed for surface chemistry in both reducing and oxidizing conditions. For the reducing model, the gas phase was chosen to be consistent with the observed composition of the ices toward the field star Elias 16 (Whittet et al. 1996; Gerakines et al. 1999), that is, $Y_{\rm H}: Y_{\rm O}: Y_{\rm CO} = 1:0.6:0.2$. For the oxidizing model, the initial composition $Y_{\rm H}: Y_{\rm O}: Y_{\rm CO} = 1:5.0:3.6$ was used (e.g., Tielens & Hagen 1982). All other parameters had the numerical values given where introduced above.

4. RESULTS

Figures 1 and 2 show, respectively, the evolution of the surface monolayer and the composition of the bulk mantle. Table 1 compares the total mantle fractions for both models



FIG. 2.—Same as Fig. 1, but for evolution in a purely reducing environment

when most of the gas phase has condensed as ice. For both models, two values of p_9 were considered because with $p_9 = 1$ the oxidizing model would predict that CO₂ will be the dominant ice mantle molecule, contrary to all observations (Ehrenfreund & Schutte 2000). For these simple models, a value of $p_9 < 1$ is the simplest remedy and is consistent with experiments and calculations (Grim & d'Hendecourt 1986; Roser et al. 2001; Ruffle & Herbst 2001) that also support a nonzero energy barrier for equation (9).

 $\label{eq:table} \begin{array}{c} \text{TABLE 1} \\ \text{Mantle Composition $H_2O:CO_2:CO$ at 10^6 yr}^a \end{array}$

Model	$p_9 = 1.0$	$p_9 = 0.1$	Elias 16
Oxidizing	100 : 110 : 51	100 : 55 : 57	100 : 15 : 25
Purely reducing	100 : 33 : 11	100 : 12 : 25	100 : 15 : 25

^a Mantle populations are scaled to H_2O being 100; p_9 is the reaction probability of CO oxidation.

The variation of the mantle composition with depth can be inferred from the evolution of the surface monolayer. In the model of Figure 1, the mantles initially grow in an oxidizing environment until reducing conditions prevail. When O/H > 1, most CO molecules arriving at the surface are converted to CO₂ and residual oxygen atoms form H₂O. Eventually O atom arrivals become so infrequent that the remaining CO molecules accrete to form pure layers in the outer mantle; most H atoms then recombine into H_2 . Thus, the mantle structure is one with CO₂ and H₂O intimately mixed in the innermost layers. Little CO is present in these layers; instead, it resides almost exclusively in the outermost layer of the mantle. This structure is consistent with that inferred for interstellar grain mantles, particularly those in the line of sight toward Elias 16 (Whittet et al. 1996; Gerakines et al. 1999). Molecular oxygen is never a major constituent of the mantles (see Vandenbussche et al. 1999).

In the purely reducing model of Figure 2, CO₂ never dominates the mantle, but this model predicts that CO and H₂O molecules should be intimately mixed throughout the mantle. Again, oxygen atom arrivals become less probable with age, CO molecules come to dominate the surface, and any subsequent O arrivals form CO₂. Hence, this leads to the prediction that both CO and CO₂ should reside together in the outer mantle, contrary to the observations.

Table 1 shows that the predicted H₂O : CO₂ : CO mantle ratios are in fact closest to the Elias 16 observations for the reducing model with $p_{0} = 0.1$, whereas those in the oxidizing model are larger than observed. While in principle there could be sources with such high CO_2 : H₂O ratios, the reason for this here is simply that CO desorption has been neglected in this model; inclusion of some nonzero nonthermal CO desorption rate, ξ_{CO} , would lower the solid-state ratios. A purely reducing model therefore cannot explain the ice mantle composition and structure toward Elias 16 as well as one in which the mantles grow in an environment with an evolving O/H ratio, the most realistic scenario. It is important to note that without the benefit of the Infrared Space Observatory data the opposite conclusion could have been drawn.

5. CONCLUSIONS

A stochastic formulation of grain surface kinetics has been developed. The calculated populations of abundant mantle species are in accord with the observed composition and structure of interstellar ices. This approach is fundamentally different from other attempts to solve this problem (Allen & Robinson 1977; Tielens & Hagen 1982; Green et al. 2001; Biham et al. 2001). The treatment given here is not a time-dependent version of the steady state Monte Carlo calculations of Tielens & Hagen (1982). Both Allen & Robinson and Tielens & Hagen used the number densities, n_i , of accreting gas-phase species to derive surface reaction probabilities; these models cannot be properly normalized. Tielens & Hagen attempted a Monte Carlo simulation and used the steady state n_i to generate the random numbers. This is not a rigorously correct simulation of the chemical master equation since the Markovian nature of chemical reactions requires the reaction probabilities follow exponential distributions, from which the (quasi) random numbers should be generated (Gillespie 1976). Other problematic issues are discussed in Charnley (2001).

A simple model can explain the composition of interstellar ices as having been formed in environments where the atomic O/H ratio evolved from oxidizing to reducing conditions. To follow the evolution for longer than an accretion time requires the specification of the mechanism and rate of nonthermal CO desorption. Inclusion of this process requires that the gas and grain chemistries be solved in tandem. This can be done by combining the kinetics described here with that of Paper I and will be reported elsewhere.

Theoretical astrochemistry at NASA Ames is supported by NASA's Origins of Solar Systems and Exobiology Programs through funds allocated by NASA Ames under interchange NCC2-1162.

REFERENCES

- Allen, M., & Robinson, G. W. 1977, ApJ, 212, 396
- Biham, O., Furman, I., Pirronello, V., & Vidali, G. 2001, ApJ, 553, 595
- Caselli, P., Hasegawa, T. I., & Herbst, E. 1998, ApJ, 495, 309
- Charnley, S. B. 1997, MNRAS, 291, 455
- 1998, ApJ, 509, L121
- -. 2001, MNRAS, submitted
- Chopard, B., et al. 1993, in Cellular Automata, ed. J. M. Perdang & A. Lejeune (Singapore: World Scientific), 157
- Ehrenfreund, P., & Schutte, W. A. 2000, in IAU Symp. 197, Astrochemistry: From Molecular Clouds to Planetary Systems, ed. Y. C. Minh & E. F. van Dishoeck (San Francisco: ASP), 135
- Feller, W. 1950, Introduction to Probability Theory and Its Applications (New York: Wiley)
- Gerakines, P. A., et al. 1999, ApJ, 522, 357
- Gillespie, D. T. 1976, J. Comput. Phys., 22, 403
- Green, N. J. B., Toniazzo, T., Pilling, M. J., Ruffle, D. P., Bell, N., & Hartquist, T. 2001, A&A, 375, 1111

- Grim, R. J. A., & d'Hendecourt, L. B. 1986, A&A, 167, 161
- Hollenbach, D. J., & Salpeter, E. E. 1970, J. Chem. Phys., 53, 79
- Lukkien, J. J., Segers, J. P. L., Hilbers, P. A. J., Gelten, R. J., & Jansen, A. P. J. 1998, Phys. Rev. E, 58, 2598
- Montroll, E. W. 1980, in Aspects of the Kinetics and Dynamics of Surface Reactions, ed. U. Landman (New York: AIP), 1
- Roser, J. E., Vidali, G., Manico, G., & Pirronello, V. 2001, ApJ, 555, L61
- Ruffle, D. P., & Herbst, E. 2001, MNRAS, 324, 1054
- Tielens, A. G. G. M., & Allamandola, L. J. 1987, in Interstellar Processes, ed. D. Hollenbach & H. Thronson (Dordrecht: Reidel), 397
- Tielens, A. G. G. M., & Charnley, S. B. 1997, Origins Life Evol. Biosphere, 27, 23
- Tielens, A. G. G. M., & Hagen, W. 1982, A&A, 114, 245
- Vandenbussche, B., et al. 1999, A&A, 346, L57
- Whittet, D. C. B., et al. 1996, A&A, 315, L357
- Willacy, K., & Millar, T. J. 1998, MNRAS, 298, 562
- Zhdanov, V. P. 1981, Surface Science, 111, 63