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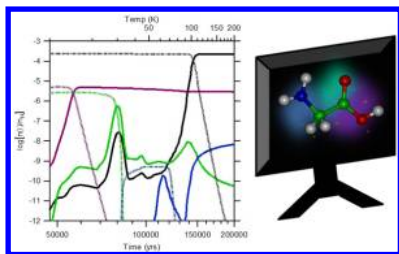
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Simulations of Hot-Core Chemistry

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1. INTRODUCTION

The most complex chemistry observed in the interstellar medium (ISM) has been observed in so-called “hot cores”, which are dense and warm regions of gas and dust within which the process of star formation is occurring.¹ A schematic of a hot core is shown in Figure 1. It is in these hot cores and their low-mass counterparts, “hot corinos”, where the chemistry of space transitions from the exotic gas-phase chemistry of cold clouds involving unsaturated species such as long hydrocarbon chains and small hydrocarbon ions, to more terrestrial-like chemistry involving saturated organic molecules such as alcohols, carboxylic acids, esters, and ethers. The various phases of chemistry that occur during the star-formation process are overviewed in Figure 2.

The molecules detected in hot-core regions can be used to trace both the chemical and physical processes that occur during the star-formation process. From a chemical perspective, the abundances, temperatures, and spatial scales of hot-core molecules offer clues about the chemical processes that are occurring as stars form. The material surrounding a new star, including the observed hot core, is incorporated into the resultant solar system and therefore may serve as the chemical starting material for planets, asteroids, and comets.¹ Studies of the molecular composition and the chemical processes that occur during star formation therefore offer clues as to the prebiotic chemical inventory available in young solar systems. From a physical perspective, the molecules present in a hot core can be used as tracers of the astrophysical processes involved in star formation. Spectral signatures of molecules can be used as diagnostic tools for temperature and density,² while abundance ratios of isotopic variants or spin states for a given molecule can indicate the physical history of the parent cloud.³ Our understanding of the star-formation process is therefore inherently linked to our ability to interpret the chemistry of hot cores. Astrochemical models that simulate chemical complexity

Special Issue: 2013 Astrochemistry

Received: March 7, 2013

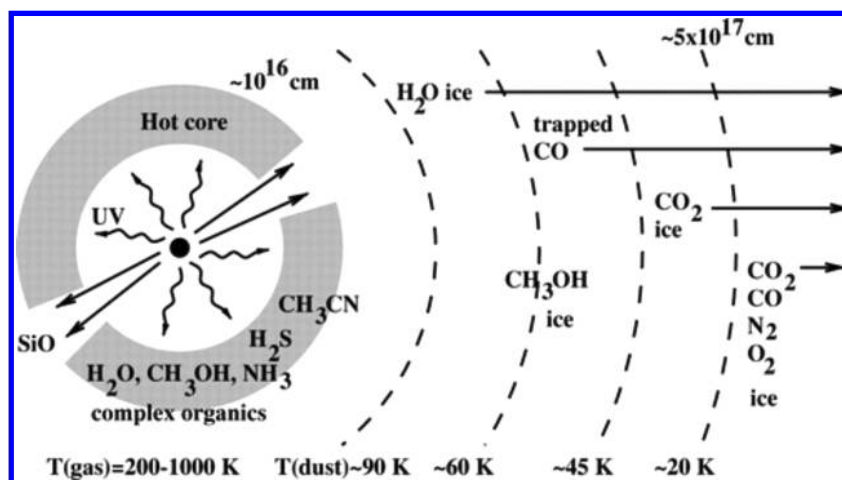


Figure 1. Schematic of a hot-core region. Reprinted with permission from ref 1. Copyright 1998 Annual Reviews.

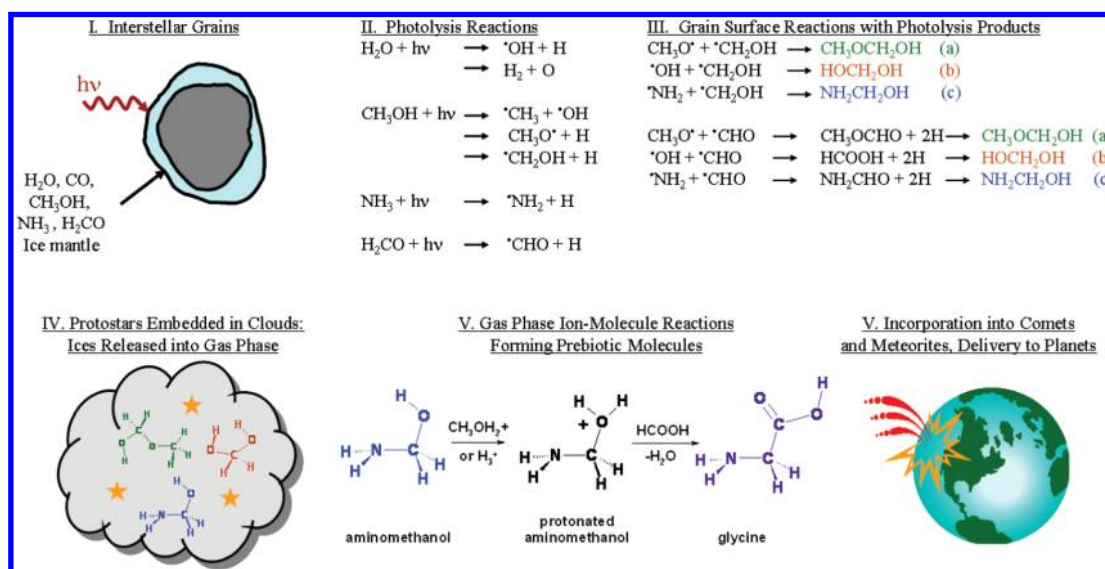


Figure 2. Overview of complex chemistry during the process of star formation. Ice chemistry on interstellar dust grains (I) dominates the chemistry in cold regions, while photo-induced and cosmic-ray-induced processes of ices (II, III) produce more complex species during the warm-up phase of a hot core. Ices are released into the gas phase (IV), where they can undergo gas-phase reactions (V) to form more complex species. Ultimately, the material present in the star-forming region gets incorporated into the solar system objects and can seed the chemistry of young planets.

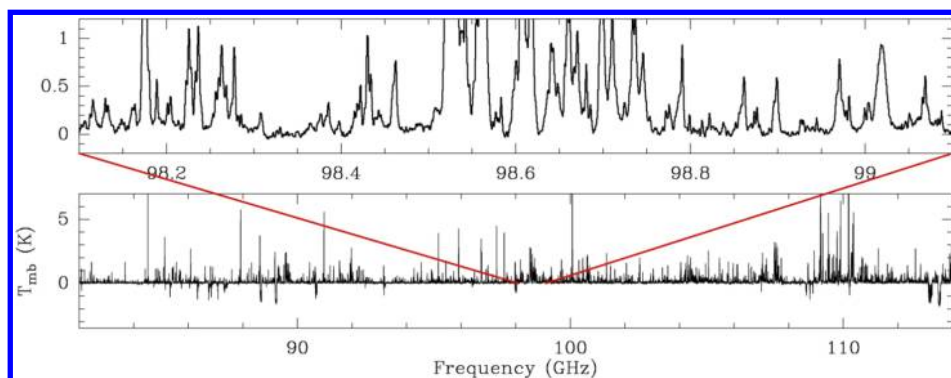


Figure 3. $\lambda = 3$ mm spectrum of the Galactic Center star-forming core Sgr B2(N), perhaps the richest such source on the sky, from observations using the IRAM 30m telescope. The upper panel shows the complexity of the spectrum in a small window of frequency space; molecular emission lines are present throughout and are frequently blended. Data were derived from ref 4. The figure was prepared by A. Belloche.

as it evolves with physical conditions are fundamental to advancement in this field of research, and as such are the topic of this review.

The primary source of information regarding the chemical state of an observed hot core is the microwave, millimeter, and submillimeter rotational emission from gas-phase molecules.

The rich molecular spectra exhibited by hot cores at these wavelengths (see Figure 3) yield abundance and excitation information for gas-phase species that are present along the line of sight of the telescope toward the astronomical source. Chemical abundances derived in this way, expressed as column densities (cm^{-2}), are representative of material that may incorporate a wide range of physical conditions over large spatial scales that are greater than 1 parsec, or 3×10^{18} cm. These spatial scales are still quite small in comparison to the distance between the source and telescope, which is more than several hundred parsecs. Furthermore, the emission from a particular molecular species is often so compact as to be spatially unresolved by the telescope; this renders uncertain the size of the emission region and thus the true column density of the molecule. There are new observational instruments, most notably the Atacama Large Millimeter Array (ALMA) interferometer, that can perform high-resolution imaging studies and will mitigate this limitation significantly. Nonetheless, it is apparent that a number of uncertainties exist in the astronomical data, even before the chemical simulation of hot-core environments is considered.

The combination within hot cores of low temperatures (typically <300 K), low densities ($n_{\text{H}} \leq 10^8 \text{ cm}^{-3}$), and changing physical conditions due to the star-formation process means that a true thermodynamic equilibrium is never achieved. Chemical simulations of hot cores are thus chiefly concerned with chemical kinetics. Several decades of work has contributed to a series of general-purpose models that are used to simulate the chemistry of a variety of interstellar source types. The chemical networks employed in these models have been adapted in recent years to examine the more complex case of hot-core chemistry.

In this paper, we discuss the most recent developments in simulations of hot-core chemistry, focusing primarily on the studies conducted in the past five years. The first section of this paper overviews the techniques used more generally in astrochemical simulations and the specific approaches employed for hot-core chemical simulations. This is followed in subsequent sections by overviews of simulations that focus on simple gas-phase chemistry applicable to all dense molecular clouds, as well as the results of more sophisticated models that simulate the complex organic chemistry of hot cores and hot corinos. Discussions of ice chemistry and biological chemistry as they pertain to hot-core simulations are also included. The paper then concludes with a discussion of comparisons between simulations and observations, with suggestions for future research directions in this area.

2. TECHNIQUES

2.1. Gas-Phase Treatments

On the basis of both observational and theoretical considerations, it is clear that gas-phase kinetics constitute a major component of the hot-core chemical system. Computational treatments of the gas phase alone are well established⁵ and inexpensive, consisting of the routine numerical integration of the set of time-dependent ordinary differential equations that govern the abundances of each chemical species. These abundances are typically expressed as fractional abundances, or concentrations, with respect to the gas number density. Hydrogen is the dominant elemental component of interstellar gas, while oxygen, nitrogen, and carbon each comprise roughly 1 part in 10^4 of gas-phase elemental abundances.⁶ Chemical

simulations of interstellar clouds commonly begin with most elements in their neutral or singly-ionized atomic state, this being an approximate representation of the chemical state of the gas under diffuse interstellar conditions. Several chemical networks are commonly used to construct the equation set, including the OSU⁷ and UMIST^{8,9} networks and variants thereof, and systematic efforts have been made recently to analyze the precision and importance of their constituent rates, as described elsewhere in this issue.¹⁰ These networks include a large range of reaction types, including various neutral–neutral reactions, ion–molecule reactions, and the electron recombination of ions, as well as ionization and photodissociation processes caused either by the ambient ultraviolet radiation field present in the ISM or by the secondary UV field induced by the collision of cosmic-ray particles with atomic and molecular hydrogen in the gas phase.¹¹ The ability of high-energy cosmic rays to penetrate deep within star-forming clouds ensures a minimum degree of ionization in the gas (typically $X_{\text{e}} > 10^{-9}$), with the resulting ions driving much of the gas-phase chemistry.

2.2. Dust-Grain Chemistry

While gas-phase simulations may produce entirely adequate results for many lower temperature interstellar environments, it has been recognized since some of the earliest observations of hot cores¹² that gas-phase chemistry alone is insufficient to reproduce observations of those objects. In particular, elevated abundances of highly saturated organic molecules such as methanol (CH_3OH) and formaldehyde (H_2CO)—as well as many more complex species such as methyl formate (HCOOCH_3), dimethyl ether (CH_3OCH_3), and ethanol ($\text{C}_2\text{H}_5\text{OH}$)—indicate the involvement of molecular material that originates on the surfaces of the dust grains that permeate the gas. Indeed, while the simulations may produce the right abundances for low-temperature environments, there are obvious omissions from the chemical network. For example, there is freeze-out onto dust grains at 10 K, and yet none of this ice chemistry is included in the standard models of these environments. It is therefore important for both cold and warm regions to include more detailed chemical networks in the simulations.

Interstellar dust grains are present throughout the molecular clouds from which high-mass stars are formed, with a gas-to-dust mass ratio of approximately 100 and a number ratio of $\sim 10^{12}$. A canonical representative dust-grain radius of $0.1 \mu\text{m}$ is frequently assumed in simulations,¹³ although the observationally determined size distribution¹⁴ frequently cited and adopted for other purposes takes the form $\text{d}N \propto r^{-3.5} \text{d}r$. However, a recent study¹⁵ found a much more complex relationship, dependent on the composition of the grain material. Additionally, Acharyya et al.¹⁶ recently investigated the effects of an explicit grain-size distribution on gas–grain models of quiescent clouds, but found no significant improvement over single-size models.

The process of star formation involves the collapse of a mass of gas and dust into a dense core to form a central protostar. The dynamics of such systems are complex and will not be discussed in detail here; however, the star-formation process results in the compression and heating of the gas during the collapse, as well as radiative heating that emanates from the central, nascent protostar. Due to the high density, the gas and dust temperatures are considered to be well coupled in hot-core sources.

During the early, cold period of molecular-cloud core evolution (with dust temperatures of ~ 10 – 20 K), the accretion of atoms and simple molecules from the gas phase onto dust grains promotes a surface chemistry that results in the buildup of icy mantles upon the grains. This ice is composed largely of water and simple hydrides, formed by the sequential addition of mobile hydrogen atoms to heavier atoms such as O, C, and N on the grain surfaces. At these low temperatures, sublimation back into the gas phase is slow compared to the accretion of new material, while the diffusion of atomic hydrogen appears to be relatively fast; for example, recent models of experimental studies of H diffusion on a CO surface found reasonable agreement when adopting a hopping barrier of 0.78 times the desorption energy.¹⁷ The diffusion of hydrogen atoms between adjacent surface-binding sites is frequently assumed in simulations to be a process of thermal hopping, although the temperature threshold between thermal and tunneling diffusion processes is still uncertain.¹⁸ While hydrides are formed on the grain surface, atomic hydrogen may also react with other hydrogen atoms accreted from the gas phase to form H_2 , which rapidly desorbs from the grain. This process typically dominates the grain-surface chemistry until such time as molecular hydrogen becomes the dominant chemical species in the gas phase, and gas-phase atomic hydrogen abundance falls away to a value closer to those of atomic carbon, oxygen, and nitrogen. Atomic species other than hydrogen may also be sufficiently mobile at low temperatures to react with each other or with the intermediary radicals that result from partial hydrogenation (such as OH, NH_2 , or CH_3). However, due to the rapidity of atomic hydrogen diffusion, and its relative abundance in the gas phase, such processes are never dominant during the early, cold phase.

Molecules formed in the gas phase, such as CO—the second most abundant interstellar molecule after H_2 —may also adhere to the grain surfaces to react with atomic hydrogen and other mobile species. Hydrogenation of grain-surface CO results in the formation of two key molecules—formaldehyde and methanol—through the sequence $CO \rightarrow HCO \rightarrow H_2CO \rightarrow CH_2OH/CH_3O \rightarrow CH_3OH$. While the other species in the sequence are radicals, and their hydrogenation is believed to proceed without impediment,¹⁹ the reaction of atomic H with both CO and H_2CO involves substantial activation energy barriers (~ 5 kcal mol⁻¹; see, e.g., ref 20). As a result, not all CO is converted to formaldehyde or methanol.

By the beginning of the hot-core stage, grain-surface-bound species such as those mentioned above represent significant, if not the main, reservoirs of O, C, and N. The molecular ices thus formed may build up mantles hundreds of monolayers thick. Surface chemistry in such environments therefore occurs mainly on the ice surfaces.

The chemical composition of interstellar dust-grain ice mantles may be determined observationally through infrared vibrational absorption spectroscopy. Observations toward the extended envelopes of young stellar objects (YSOs), within which hot-core sources typically reside, indicate compositions such as those shown in Table 1. Water is the most abundant ice component, followed by CO and CO_2 , with methane and ammonia also attaining substantial abundances with respect to water.

The large quantities of CO that are deposited onto the dust grains from the gas phase allow the production of significant quantities of methanol by sequential hydrogenation. The degree of CO-to- CH_3OH conversion appears to be greater

Table 1. Typical Molecular Abundances in Ices for Several Source Types As Based on Ref 21, Compared to Results from Modeling Studies from Refs 22 and 23^a

molecule	abundances of ice species determined from Spitzer observations of YSOs ²¹			model results for cloud collapse phase	
	low-mass YSOs	high-mass YSOs	background stars	gas–grain simulations ²²	Monte Carlo simulations ²³
H_2O	100	100	100	100	100
CO	29	13	31	19	42
CO_2	29	13	38	4.1	24
CH_3OH	3	4	4	1.5	5
NH_3	5	5		25	21
CH_4	5	2		2.2	9

^aThe abundances are given as percentages relative to water; for reference, the typical column density of water ice in these sources is $\sim 10^{18}$ cm⁻².²¹

toward star-forming sources than is found in quiescent molecular-cloud regions, which are usually considered to be less chemically evolved. Recent Spitzer Space Telescope observations identified some YSOs with methanol ice abundances as high as 30% with respect to water.²⁴

Millimeter and submillimeter observations of hot cores show molecular rotational emission with excitation temperatures (commonly referred to as rotational temperatures) typically greater than 100 K, as well as abundances of gas-phase species, such as methanol, that are comparable to those observed in the solid phase in YSO envelopes. The implication is thus that the high gas-phase abundances are caused by the sublimation of the hydride-rich ices that coat the dust grains, caused by the elevated temperatures attained during the star-formation process.

Some of the molecules detected in the gas phase toward hot cores—in particular, methanol—are directly detected in the ices in YSO envelopes, with comparable abundances, indicating that they represent material sublimated from the icy grain mantles that formed at an earlier stage. However, infrared absorption observations of ice mantles typically yield upper limits no lower than $\sim 1\%$ of water ice abundance for the other ice components, corresponding to around 10^{-6} of total hydrogen; most gas-phase hot-core molecules (especially complex organics) are present at abundances that are several orders of magnitude lower than this. The presence of a solid-phase precursor for such molecules cannot therefore be ascertained. For this reason, it has been unclear whether the increasingly complex organic molecules that are detected toward hot cores have been simply sublimated from the grains, or whether they are formed by gas-phase chemical processes fueled by the release of simpler species from the grain surfaces. Until recently, this latter view had prevailed for several reasons. First, gas-phase models of the post-sublimation phase of hot-core chemistry could reproduce adequately the abundances of most molecules included in the chemical networks.^{5,25–27} Second, the existing models of grain-surface chemistry were intended to simulate the low-temperature conditions of quiescent molecular clouds, in which hydrogen is the dominant surface reactant and the reaction products are mainly limited to simple hydrides; those models did not therefore predict significant production of more complex species. Third, the surface physics and chemistry of interstellar dust grains are poorly defined, especially for the low temperatures involved,

when compared with the gas-phase chemistry, and the accurate simulation of even the buildup of simple dust-grain ice mantles is challenging.

Several new simulation techniques have been developed over recent years that address some of the problems and limitations of combined gas-phase and dust-grain chemical modeling, while experimental studies have shown that many of the more complex species detected toward hot cores may be formed within or upon laboratory ices similar to those found in the ISM, under irradiation from ultraviolet sources or bombardment with high-energy particles that mimic the action of cosmic rays. However, equally compelling have been new measurements of gas-phase reaction rates, showing that some of the key reactions involved in the conversion of simple sublimated molecules into more complex hot-core species are far less efficient than previously thought.

Many of the recent developments in the simulation of hot-core chemistry, and in the associated experimental and observational science, indicate that the interactions between the gas-phase and the dust-grain ice mantles are more complex than previously thought. The simple picture of material transfer from one phase to another may be less accurate than a system of continuously interacting gas and surface chemistry, deposition, and sublimation.

3. SIMULATION METHODS

Various methods now exist for chemical kinetics simulations applicable to hot-core chemistry. Such models fall into two major groups, those that explicitly model both gas-phase and grain-surface chemical processes and the exchange of material between the two phases (so-called “gas–grain” models) and those that either treat gas-phase chemistry alone or combine it with empirical treatments of grain-surface chemistry and/or gas–grain coupling. Due to the importance of grain-surface processes to hot-core chemistry, more discussion will be given to the former category.

3.1. Gas-Phase and Quasi-Gas–Grain Models

Pure gas-phase models are now rarely used for the simulation of hot-core chemistry. However, models that combine full gas-phase kinetics with a system of “freeze-out” of gas-phase material into an inert reservoir of dust-grain ices have been used frequently in recent years, in particular by Viti and co-workers;^{26,28,29} we will refer to such models here as “quasi-gas–grain” models, as they include only a partial or empirical coupling between the two chemical phases and typically exclude an explicit treatment of surface reactions. In these models, the accretion of gas-phase species onto the dust grains results in their conversion into the most likely solid-phase products, typically hydrides, with molecules such as CO being converted to fixed proportions of the several hydrogenation states that they may assume in the ices (i.e., CO, H₂CO, or CH₃OH). Most molecules are otherwise assumed to remain in their previous chemical state when transferred to the solid phase. This approach has some advantages over models that explicitly simulate grain-surface chemistry (see below), insofar as the degree of solid-phase processing may be controlled directly on an empirical basis, guided by astronomical observations. Furthermore, these models have been combined with the results of temperature-programmed desorption (TPD) experiments³⁰ to extrapolate the measured desorption characteristics of various ice mixtures to astronomical warm-up time scales. Such an approach allows complex phase changes within the ices

during warming to be included; explicit gas–grain models cannot currently reproduce such behavior, due to the lack of a compatible microscopic treatment for phase changes.

The limitations of the method include the lack of a continually interacting gas-phase and grain-surface chemistry. For example, the release of a fraction of grain-surface-formed methanol into the gas phase has recently been invoked as an explanation for the presence of gas-phase methanol in quiescent regions,³¹ following recent measurements of gas-phase rates that suggest that gas-phase processes alone are prohibitively slow.^{32,33} A cycle of continuous grain-surface adsorption, processing, and return to the gas phase may also be important to the chemistry of simple molecules during the warm-up phase of a hot core.

The use of such models by Viti and Williams,²⁶ who included thermal evaporation rates for molecules in the ice reservoir, demonstrated the importance to gas-phase chemistry of the differential release of simple molecules of varying surface-binding strengths during the gradual warm-up of the hot core; previous models had typically assumed a near-instantaneous evaporation of ice mantles into the gas phase. The incorporation of laboratory TPD data³⁰ into this model, by Viti et al.,²⁹ further affirmed the necessity of such time- and temperature-dependent considerations in hot-core chemical models (see also section 7.9).

Similar quasi-gas–grain methods have more recently been used to model the formation of methyl formate (HCOOCH₃) within the dust-grain ices at low temperatures,³⁴ through cosmic-ray-induced processes whose rates have been measured in the laboratory.³⁵ The model introduced a single reaction between solid-phase CO and CH₃OH, adopting a fixed rate (see section 7.5). The results demonstrated that other processes would be required to reproduce observed methyl formate abundances in hot cores. This approach was extended to include several gas-phase and solid-phase reaction mechanisms, using empirical rates, to explore the parameter space of various low-temperature mechanisms for the formation of interstellar glycolaldehyde (HOCH₂CHO).³⁶ While gas-phase mechanisms were ruled out, several routes for low-temperature formation of glycolaldehyde were deemed plausible.

While such quasi-gas–grain methods may be effective in the analysis of low-temperature solid-phase chemistry, especially where incorporating well-defined experimental rates, the warm grain-surface/ice chemistry expected in star-forming regions may be too complex for methods that do not explicitly model a broad network of reactions and processes.

3.2. Gas–Grain Models

Gas–grain chemical models explicitly treat the chemical kinetics of both the gas phase and the grain/ice surface, as well as in some cases the chemistry of the bulk-ice mantle. Within this category, several subsets exist, which vary primarily in their treatment of the grain-surface kinetics.

3.2.1. Rate Equations. The set of ordinary differential equations that describes the gas-phase chemical kinetics is easily solved using publicly available solver routines to produce time-dependent abundance information for each chemical species, even under the changing physical conditions of the collapse and warm-up of the hot core. For this reason, most current gas–grain hot-core models employ this method, extending it to the treatment of grain-surface chemistry. In such simulations, the grain-surface population of each chemical species is governed

by the evolution of a set of reaction rates, as well as loss and gain rates associated with thermal and nonthermal evaporation mechanisms and accretion of gas-phase material, respectively. Second-order surface reaction rates (R_{AB}) are typically assigned a rate coefficient (k_{AB}) that is dependent on the rate of surface hopping of each reacting species; thus

$$R_{AB} = k_{AB}N_A N_B \quad (1)$$

$$k_{AB} = \kappa_{AB}[k_{\text{hop}}(A) + k_{\text{hop}}(B)]/N_s \quad (2)$$

where N_i is the individual population of species i on a grain, N_s is the number of binding sites on the surface of the grain, typically assumed to be around 10^6 for a dust grain of $0.1 \mu\text{m}$ size, and κ_{AB} is an efficiency that takes into account the activation energy barrier of the reaction where one exists. The individual hopping rates are typically defined as

$$k_{\text{hop}}(A) = \nu_A \exp[-E_{\text{hop}}(A)/kT] \quad (3)$$

where ν_A is a characteristic vibrational frequency for the species in question. The hopping barriers are representative values assigned for the binding of species i to a specific surface; no local binding information is taken into account, as the model itself considers only the population (or, alternatively, concentration) of each species on the grain, and not their physical locations. Other hopping expressions are also used for the case where hydrogen atoms may tunnel through the barrier. The rate coefficient for thermal evaporation is formulated similarly to that for thermal hopping, and the diffusion barrier is frequently taken to be a fixed proportion of the total binding energy, usually in the 0.3–0.8 range. Methods such as this have been used for some years—notably, in the case of hot-core chemistry, by Caselli et al.³⁷

The use of the simple rate-equation approach is popular in the simulation of interstellar chemistry in general and produces plausible chemical abundances for most species that may be observed toward hot cores (other uncertainties in the models notwithstanding); however, it suffers from several shortcomings, which are discussed below, along with the methods currently being used to address or avoid them.

3.2.2. Modified Rate Equations. The main shortcoming of the rate-equation method as applied to gas–grain chemical models is that the grain-surface chemistry is by definition a stochastic process. While rate-equation simulations may behave well if reactant populations are large, in the case where the populations of individual species are on the order of unity (i.e., one atom or molecule per grain), the probabilistic nature of the chemistry may become critical to one or all of the reactant or product populations. In practice, the effect on the production of important observable grain-mantle species is often rather small, in spite of inaccurate abundances for the reactant species, most notably atomic hydrogen. However, the magnitude of the inaccuracies is generally difficult to quantify, especially among less abundant species.

Attempts were made by Caselli, Herbst, and co-workers^{38,39} to remedy the inaccuracies of the rate-equation method by adjusting the rate coefficient of the reaction (eq 2) in a semi-empirical fashion to limit the reaction rates of hydrogen atoms to the rate at which they are deposited on the grain surface, or the rate at which they evaporate, depending on which process should dominate the surface reaction kinetics of atomic H. This method produced only mixed success; however, the more recent, and somewhat different, method proposed by Garrod⁴⁰ has been shown to produce excellent agreement with exact

Monte Carlo treatments (see below) of the same chemical network over a wide range of physical conditions.⁴¹ This approach addresses stochastic effects on every surface reaction adaptively according to the formation rates of the reactants and the degree of competition between the reaction and other surface processes. Moderate inaccuracies occur where simultaneous production of competing reactants occurs (e.g., under conditions of strong UV-induced photodissociation of surface material), or where the reaction network used is incomplete (i.e., if important reactions are omitted). The method has recently been incorporated into the hot-core model of Garrod,⁴² which will be described in more detail below.

3.2.3. Exact Stochastic Methods. The use of exact methods in the simulation of stochastic chemistry is typically far more demanding of CPU time than the equivalent models based on the integration of ordinary differential equations, and the coupling of gas-phase and grain-surface processes using such approaches is technically challenging. Therefore, few such exact methods have ever been applied to hot-core chemistry.

The most comprehensive and precise kinetic models of interstellar surface chemistry in use at present, devised by Cuppen,⁴³ model the individual motions of atoms on the dust grains within a fixed lattice. While this microscopic Monte Carlo approach provides useful information regarding the locations of each species (within a fixed physical structure), as well as treats surface binding according to the local surface composition, many more calculations per surface reaction are required than in any other type of model, and at present no gas-phase chemistry is included in the simulations. Such models have not yet therefore been applied to hot-core chemistry.

Vasyunin et al.⁴⁴ recently produced a model that solves the master equation for the combined gas-phase and surface chemistry using Monte Carlo techniques in a fashion similar to that of Charnley.⁴⁵ The model adopts a standard gas-phase network and averaged grain-surface reaction rates (i.e., eqs 2 and 3), producing exact (integer) gas-phase and grain-surface populations for each chemical species, albeit without the structural information inherent in the microscopic models of Cuppen. This stochastic approach therefore entirely avoids the problems associated with rate equations. The model has since been developed to handle a three-phase approach, which will be described in more detail below.

3.2.4. Three-Phase and Multiphase Models. The use of the rate-equation approach in the modeling of the growth of dust-grain ice mantles derives from earlier models that treated simple diffusive surface chemistry on the assumption that products (typically H_2) would evaporate immediately upon formation. However, the use of such models to simulate environments in which substantial ice mantles form on the grains produces a logical inconsistency; in the case that more than one monolayer of molecular material builds up on the surface of the dust grain, the populations of each individual species become representative not only of the surface ice layer but of the material underneath, while the reaction rates are based only on an assumption of surface diffusion. The detailed form of the reaction rates may be adjusted to account for this layering effect through an alternative calculation of the number of binding sites, N_s , but the model will provide no information as to the stratification and preservation of different granular ice layers.

A so-called “three-phase” chemical model, consisting of gas-phase, grain/ice-surface, and bulk-ice-mantle populations, was devised by Hasegawa and Herbst⁴⁶ for application to dark cloud

chemistry, and this approach has more recently been adopted by others.^{47,48} Variations of the method have been used to model hot-core chemistry explicitly, by Vasyunin and Herbst,²³ adopting the stochastic method mentioned above, and by Garrod.⁴² However, there is evidence from experiment that processes such as atomic hydrogen diffusion and molecular photodesorption are active to depths of several monolayers into the ice,^{17,49} and the thermal segregation of bulk-ice material may also make a precise treatment of subsurface processes difficult using even a three-phase approach.

The “multiphase” model of Vasyunin and Herbst²³ uses a three-phase approach, but with memory of each layer as it forms, allowing later evaporation of the same material to be traced in the order in which it was deposited. The three-phase model of Garrod⁴² introduces an active chemistry within the bulk ice, so that the combined surface and bulk-ice chemistry is treated separately and self-consistently—although the physical and chemical parameters relating to the bulk-ice diffusion are as yet poorly defined. The model assumes that thermal diffusion may occur in the ice mantle (and between the mantle and surface populations) through a swapping process, as suggested by Öberg and co-workers,⁵⁰ assuming rates similar in form to the surface rates. These bulk-diffusion processes only become important at the elevated temperatures found under hot-core conditions.

4. CHEMICAL PARAMETERS

4.1. Initial Elemental Abundances

Models of hot-core chemistry, and interstellar chemistry in general, typically include species composed of H, He, C, N, O, S, Si, and a selection of metals including Mg and Na. Other elements such as F and P are also present to a limited degree in some chemical networks, based on related interstellar molecular detections.^{51–53} The abundances of C, N, O, and S (with respect to total hydrogen) adopted in models are largely based on observational values for diffuse interstellar clouds.⁶ In such environments, these elements are expected to be present mainly as atoms or atomic ions and may be directly detected in those forms. In general, the chemistry of the heavier metals included in the networks is sparse; due to their low ionization energies, their main function in the models is to provide an appropriate quantity of gas-phase electrons, obtained through photoionization. The number and precise quantity of heavy metals in the models may therefore be chosen empirically to control the ionization fraction in the gas. For this reason, so-called “low-metal” abundances⁵⁴ are frequently chosen for hot-core and other chemical models. Helium, while unable to be directly photoionized by the interstellar radiation field (see section 4.2), may be ionized by collisions with cosmic-ray particles, allowing the resulting He⁺ ions to participate in destructive electron-transfer reactions with gas-phase molecules. Initial elemental abundances used in a recent hot-core chemical model may be found in Table 2.

The majority of the observed diffuse-cloud abundances of C, N, and O are found to approximately correspond with the aggregated abundances in denser regions of molecules bearing those respective atoms based on the dominant molecular carriers of these atoms. In particular, the abundances of gas-phase CO and solid-phase water are consistent with diffuse-cloud elemental abundances. The abundance of N₂, the most prevalent form of interstellar gas-phase nitrogen, cannot be ascertained directly through pure rotational spectroscopy (due

Table 2. Typical Initial Elemental/Molecular Abundances (With Respect to Total Hydrogen) Used in Chemical Models of Hot Cores^a

molecule	initial elemental/ molecular abundance	molecule	initial elemental/ molecular abundance	molecule	initial elemental/ molecular abundance
H	0.3	O	3.2E−4	P	3.0E−9
H ₂	0.3	S	8.0E−8	Cl	4.0E−9
He	0.09	Na	2.0E−8	Fe	3.0E−9
C	1.4E−4	Mg	7.0E−9		
N	7.5E−5	Si	8.0E−9		

^aTaken from ref 22. Values are based on the low-metal abundances of Graedel et al.⁵⁴ and more recent determinations of diffuse cloud abundances; see ref 61 and references therein. A discussion of the use of different elemental abundances in chemical models may be found in ref 62.

to the absence of a permanent dipole moment), but may be inferred by observation of N₂H⁺. Solid-phase ammonia abundances are also sufficiently large toward some sources to be detectable through infrared absorption spectroscopy, in such cases comprising a large proportion of the diffuse-cloud elemental value for nitrogen. However, the sulfur budget inferred from observations of sulfur-bearing species toward hot cores (and other dense regions) does not tally with the diffuse-cloud value. Likewise, H₂S, the expected dominant form of solid-phase sulfur, has not been reliably identified in interstellar infrared spectra. Furthermore, chemical models that use the full diffuse-cloud initial abundance of sulfur produce abundances of sulfur-bearing species that are sometimes several orders of magnitude greater than those observed. It is currently unclear in what form the sulfur resides in dense regions, such that most of it would be unavailable for chemistry in the hot phase; recent suggestions⁵⁵ for the missing form of sulfur include sulfur polymers and polysulfanes (H₂S_n). Consequently, most recent hot-core models have adopted low initial sulfur abundances, based on the work of Graedel et al.⁵⁴ Early suggestions⁵⁶ that sulfur-bearing molecules could act as observational chemical clocks for hot cores and massive YSOs have so far been frustrated by the uncertainties in total sulfur abundances, the effects of uncertain physical conditions on the sulfur-related chemistry, and the lack of experimental data for gas-phase reactions.^{57–59} Grain-surface chemical networks also include little sulfur chemistry in comparison to the equivalent oxygen-related networks, although there may be observational evidence⁶⁰ to suggest differences in the chemical behavior of methyl mercaptan (CH₃SH), which is not currently included in grain-surface networks, and its oxygen-bearing equivalent, methanol, which is formed substantially by grain-surface chemistry.

4.2. Gas-Phase Chemistry

Direct UV photoionization or photodissociation by the ambient interstellar radiation field (ISRF) is restricted to processes requiring photon energies of <13.6 eV, beyond which limit all photons are effectively extinguished through absorption by interstellar atomic H. However, in the dense gas within hot cores, all external UV and visible radiation is expected to be extinguished. In the gas phase, the majority of ionization and photodissociation (see Table 3, process types 1 and 2) is caused by the secondary field induced by cosmic-ray collisions with hydrogen atoms and molecules,¹¹ which radiate in the UV.

Table 3. Typical Rates for a Selection of Generic Gas-Phase Reactions and Photoprocesses Important to Hot-Core Chemistry^a

type no.	reaction/process type	generic reaction/process	typical rate coefficient
1	CR-induced photoionization	$X + h\nu \rightarrow X^+$	$10^3 \zeta_0 \text{ s}^{-1}$
2	CR-induced photodissociation	$XY + h\nu \rightarrow X + Y$	$10^3 \zeta_0 \text{ s}^{-1}$
3	elimination/condensation	$XY^+ + AB \rightarrow XA^+ + YB$	$10^{-9}(T/300 \text{ K})^{-0.5} \text{ cm}^3 \text{ s}^{-1}$
4	protonation	$XH^+ + A \rightarrow X + AH^+$	$10^{-9}(T/300 \text{ K})^{-0.5} \text{ cm}^3 \text{ s}^{-1}$
5	charge transfer	$X^+ + A \rightarrow X + A^+$	$10^{-9}(T/300 \text{ K})^{-0.5} \text{ cm}^3 \text{ s}^{-1}$
6	dissociative charge transfer	$X^+ + AB \rightarrow X + A^+ + B$	$10^{-9}(T/300 \text{ K})^{-0.5} \text{ cm}^3 \text{ s}^{-1}$
7	dissociative recombination	$XH^+ + e^- \rightarrow X + H (\sim 5\%)$ $XH^+ + e^- \rightarrow \text{other products } (\sim 95\%)$	$10^{-7}(T/300 \text{ K})^{-0.5} \text{ cm}^3 \text{ s}^{-1}$
8	radiative association	$X^+ + A \rightarrow XA^+ + h\nu$	$<10^{-12}(T/300 \text{ K})^{-2} \text{ cm}^3 \text{ s}^{-1}$
9	neutral exchange	$XY + AB \rightarrow XA + YB$	$10^{-10} \text{ cm}^3 \text{ s}^{-1}$

^aX, Y, A, and B are generic; H represents atomic hydrogen. The interstellar cosmic-ray ionization rate is typically assumed to take a value $\zeta_0 \approx 10^{-17} \text{ s}^{-1}$.

Following the desorption of ice mantles at high temperatures, the main destruction mechanism for gas-phase molecules is typically protonation by abundant molecular ions such as H_3^+ , H_3O^+ , or HCO^+ , followed by dissociative recombination with electrons (see Table 3, reaction types 4 and 7). Recent models^{22,42,63,64} have incorporated the results of Geppert and co-workers³³ to assume low efficiencies for the re-formation of complex molecules following electronic recombination of their protonated forms, as indicated in Table 3. Reaction of complex molecules with atomic ions H^+ and He^+ typically results in dissociation (reaction type 6).

Besides the destruction of complex molecules, gas-phase formation processes also exist. In particular, the protonation (reaction type 4) of grain-surface-formed molecules such as formaldehyde, methanol, and formic acid produces molecular ions that may further react with other gas-phase organics to produce larger molecules, either by elimination/condensation reactions or by radiative association (reaction types 3 and 8). The latter process is typically at least several orders of magnitude slower than other ion–molecule reactions (and shows extreme variability, case by case), as the reaction efficiency is dependent on competition between photon emission and redissociation of the complex. The former process had been assumed until recently to be responsible for the formation of complex species such as methyl formate; however, in that case, the reaction between formaldehyde and protonated methanol, producing protonated methyl formate and H_2 , was found by calculation to be highly inefficient⁶⁵ (see also section 7.1). Combined with the expected low efficiencies for dissociative recombination that would retain complex molecular structure,³³ it is questionable whether such processes can achieve the requisite abundances of complex organics in hot cores, aside from certain specific examples such as dimethyl

ether.^{22,63} It is nevertheless plausible that other individual cases exist for which gas-phase formation may be plausible.

Neutral–neutral exchange reactions may also play a role in gas-phase complex-molecule production; formic acid may be formed in this way by the reaction between formaldehyde and the OH radical. However, possible formation routes for larger molecules are only beginning to be investigated.⁶⁶

Neutral–neutral and ion–molecule reactions are effective, nevertheless, in the chemistry of simple gas-phase molecules in hot cores; for example, models⁵⁶ indicate that such processes lead to the proliferation of various sulfur-bearing molecules (e.g., CS, SO, and SO_2) following sublimation of H_2S from the dust grains (see section 4.1). See ref 10 (this issue) for further discussion of gas-phase processes involving simple species.

Several gas-phase chemical networks are commonly used for interstellar chemistry in general, such as the UMIST^{8,9} and OSU⁷ networks and the KIDA database,⁶⁷ and will not be discussed further here. However, some recent gas–grain chemical models^{4,22,42,63,64} have included new species to be formed on dust-grain surfaces, but for which no gas-phase reaction data currently exist. These models have usually assumed typical, representative values for the relevant classes of reaction most likely to result in destruction of the molecule, or have used simple methods based on dipole moments and polarizabilities, for thermodynamically viable ion–molecule reactions. While the inclusion of these “bare-minimum” reaction sets is necessary to investigate the behavior of certain complex organic molecules (COMs), it should be borne in mind that little of the gas-phase chemistry appropriate to large molecular ions and neutrals has been investigated experimentally, and it is plausible that specific state-to-state reaction rates may be important in the case of complex species.^{64,68}

4.3. Grain-Surface and Ice Chemistry

The key chemical parameters associated with the dust-grain chemistry in hot-core models are the binding energies (also labeled “desorption energies”) and diffusion barriers employed in the calculation of the grain-surface desorption and reaction rates (see eqs 1–3). Older models have typically concentrated on bare dust-grain-surface values, represented by silicate or graphite surfaces, or used a mixture of grain-surface and ice-surface values for each chemical species in the model, with water ice being most typically used for the ice-surface values. Recent models^{22,63} have made use of TPD desorption data provided by Collings et al. (2004)³⁰ to obtain desorption energies (E_{des}) for a small selection of important, stable interstellar molecules. However, values for atoms and radicals are more difficult to obtain, due to their short laboratory lifetimes. Current models typically retain the values of Tielens and Allamandola⁶⁹ for C, N, O, and S atoms on water ice (uniformly, $E_{\text{des}} = 800 \text{ K}$, or 6.65 kJ mol^{-1}). Garrod and Herbst⁶³ constructed a set of binding energies, based around the experimental values of Collings, to represent an amorphous water ice surface. Missing values corresponding to radicals or stable molecules for which no data existed were calculated by simple interpolation or extrapolation from the known values, typically assuming the binding energies of molecular functional groups or atoms could be added or subtracted linearly; this allowed molecules with strong hydrogen-bonding properties to be treated self-consistently in the absence of measured values. This set of binding energies was used again and further developed in later models.^{4,22,42} The choice of these values plays a major part in the high-temperature behavior of complex

organics; the observed spatial temperature gradients in hot cores will result in the desorption of differently bound molecules in different locations.

The choice of diffusion barrier between binding sites on a given surface for any individual species, as employed in the surface reaction rates, is typically assumed to be a fixed proportion of its binding energy. Values in the ~ 0.3 – 0.8 range are commonly adopted. However, there is little agreement as to which may be most appropriate for any particular case; errors on experimentally determined values are typically large (i.e., $>10\%$), due partly to the range of binding strengths caused by surface inhomogeneities.^{43,70} In the case of atomic hydrogen, the problem is further complicated by the possibility of tunneling through the barriers at temperatures around 10 K. On the basis of the work of Katz et al.,⁷¹ most hot-core models, and gas–grain models in general, assume that hydrogen tunneling is less efficient than thermal hopping. However, when models that explicitly treat the stochastic nature of the surface chemistry are used, the rapidity of hydrogen diffusion may cease to be the rate-limiting step in surface hydrogenation (which would depend rather on the rate of accretion of atoms from the gas phase), rendering the precise determination of the hydrogen diffusion rate less important to the model results.

It is likely that the most important limitation on the accuracy of grain-surface chemical models that use a generalized surface binding energy value for each species is the very assumption of a single value, which cannot account for the occasional trapping of surface species in deep potential wells.⁷² The bulk-ice-diffusion characteristics employed in the model of Garrod⁴² are yet even less well-defined by experiment, although there are ongoing efforts to constrain chemical models using data from the methanol photolysis experiments of Öberg et al.,⁷³ which were found to rely explicitly on bulk-ice processes as well as surface chemical mechanisms.

A full treatment of the dust-grain ice chemistry also requires the definition of activation energy barrier parameters. Unfortunately, there exist very few estimates of such parameters that directly address ice chemistry; furthermore, at the low temperatures (~ 10 K) at which many important grain-surface species are formed, passage through the activation energy barrier may be mediated by quantum tunneling. When treating tunneling reactions on the ices, astrochemical models have typically assumed a square-well potential of uniform 1 Å width,¹³ adopting a barrier height derived from gas-phase measurements. Recent quantum-chemical rate calculations for the critically important surface reactions $\text{H} + \text{CO}$ and $\text{H} + \text{H}_2\text{CO}$ have shown^{74,75} that the adoption of the square-well potential, with a uniform barrier width, may produce tunneling rates that are some orders of magnitude different from those obtained from the exact, multidimensional calculations, while the presence of an ice surface may alter both the rate and product-branching of the reaction. It is unclear how important such effects are for the rates of reactions involving species much heavier than atomic H, as both thermal and tunneling rates are likely to be prohibitively small at extremely low temperatures, such that in either case the reaction should have little influence on the overall chemistry compared with other processes.

Aside from the few barrier-mediated reactions for which there exist either calculated or experimentally determined rates, activation energies based on gas-phase rates are typically assumed; a large number of such values have been collated or interpolated (using the Evans–Polanyi relationship) by Garrod,⁴² for ice reactions important to hot-core chemistry.

Taquet et al.⁴⁸ have also published calculated transmission probabilities for a selection of hydrogen- and deuterium-related barrier-mediated reactions, based on Eckart potentials.

In typical hot-core chemical models, thermal (in the form of a Boltzmann function) or tunneling calculations are used to produce a reaction/transmission probability where a barrier exists. In many models, this efficiency has been directly applied to the reaction rate coefficient (through the parameter κ_{AB} in eq 2);^{4,13,22,63,64} however, as made clear by Tielens and Hagen,⁷⁶ the lifetime against diffusion out of the binding site for each reactant must also be considered. More recent models^{42,47,77} have again considered the competition between reaction and diffusion, albeit in a very simple manner, taking the efficiency factor κ_{AB} as the ratio of the reaction rate to the sum of the competing rates. This difference in treatments alone can account for orders of magnitude differences in reaction rates. In cases where barrier-mediated reaction is faster than diffusion out of the binding site by one or other reactant, this would lead to a reaction efficiency close to unity. Conversely, under conditions of rapid diffusion, the reaction rate would tend toward the transmission rate, becoming insensitive to the rates of diffusion. Such considerations should also be borne in mind when determining activation energy barrier parameters from experimental kinetics. However, the approach used currently for reaction-diffusion competition nevertheless simplifies the system, using the same generalized diffusion parameters as elsewhere in the model, thus ignoring binding interactions between the reacting species.

As described above, the accurate treatment of grain-surface barrier-mediated reaction rates presents a great challenge, which perhaps may only be adequately addressed by very specific quantum-chemical simulations of each reaction system, with explicit consideration of the binding surface.

5. PHYSICAL CONDITIONS

Gas densities within hot cores are typically considered to fall in the 10^5 – 10^8 cm^{-3} range, although many single-point models adopt values of around 10^7 cm^{-3} . Power-law density and dust temperature gradients have been determined for specific sources by modeling dust or molecular emission data.^{78,79} Gas kinetic temperatures may also be inferred from the excitation temperatures obtained from molecular emission. In the warm region of the core, densities are sufficiently high that the gas and dust temperatures are effectively coupled.⁸⁰ Past models have frequently used two temperature values to model the hot-core chemistry, a low value (~ 10 K) corresponding to the early stage of ice formation and a high value of 100 K or more corresponding to the later, hot stage. The cold stage has often been accompanied by an isothermal collapse model,⁵ allowing the core to progress from diffuse or translucent-cloud conditions to a denser state. The hot stage has usually begun with the instantaneous ejection of the simulated grain mantles into the gas phase.

Recent models have included more complex temperature treatments for the collapse phase; Garrod⁴² allows the dust temperature to fall from ~ 18 to 8 K as the cloud collapses, by considering the balance between heating from the external radiation field and thermal emission from the grains, following the work of Garrod and Pauly.⁴⁷ Vasyunin and Herbst²³ have also adopted an empirical relationship to treat this effect. The main reason for such an approach is that the formation of grain-surface CO_2 appears to require dust temperatures greater than

around 12 K to produce the significant quantities observed in interstellar ice mantles.⁴⁷

Viti and Williams²⁶ were the first to introduce a true time dependence to the temperature of the hot core, allowing the core to warm gradually; in this model and the follow-up work of Viti et al.,²⁸ the purpose was to trace the time dependence of molecular desorption from the grains. Garrod and Herbst⁶³ used a similar approach to investigate the temperature-dependent behavior of grain-surface chemistry during warm-up, and the same approach has been used again by other authors.^{4,22,42,64} Viti et al.²⁹ used power-law warm-up profiles, guided by observational data on protostellar switch-on times, which ranged from around 10^4 to 10^6 years depending on the stellar mass.

Other physical parameters considered in the models include the cosmic-ray ionization rate and the size parameters of the dust grains. Neither of these has yet been investigated in great detail in the context of full gas–grain chemical models of hot cores.

6. SIMPLE MOLECULES

The chemical behavior of simple molecules (i.e., <6 atoms) in hot cores, and in the interstellar medium in general, is rather better understood than that of more complex species, due mainly to the greater amount of experimental data available on the relevant gas-phase reactions. As such, the chemistry of simple molecules, especially in the context of gas-phase chemistry, will not be discussed in detail here.

While a large and diverse assortment of simple molecules have been detected in various interstellar regions, hot cores are nevertheless replete with simple species as well as the more complex molecules that contribute so much to their rich emission spectra. The high temperatures attained in hot cores release a number of simple, fully hydrogenated molecules into the gas phase, such as H_2O , NH_3 , H_2CO , and H_2S . Neutral–neutral and ion–molecule reactions in the gas phase act to convert these molecules to other simple products.^{12,25,56,81,82} Simple species detected toward hot cores include CO, HCO^+ , HCN, HNC, HNCO, CS, SO, and SO_2 .

The abundances of sulfur-bearing species appear to be dependent on the release of H_2S from the grains at high temperatures.^{26,56,58} For this reason, sulfur chemistry has been mooted as a means of tracing the dynamical history of a hot core;⁵⁶ however, as mentioned above, the precise form that sulfur takes on grain surfaces is unclear, and it is likely that H_2S contains only a fraction of this total, based on the sulfur budget of diffuse interstellar clouds. Observations suggest OCS may be an alternative carrier of sulfur in ices.⁸³

Nitrogen-bearing species are routinely detected toward hot cores. In the case of HCN, rotational temperatures of many hundreds of Kelvin are observed in some sources. Rolffs and co-workers⁸⁴ used emission from this molecule to constrain the physical structure of hot-core source G10.47+0.03. These authors also inferred an HCN fractional abundance in the hot regions of around 10^{-5} with respect to H_2 . Although current (non-source-specific) models do not produce quite such high values,^{22,42} HCN appears to be formed in the hot gas phase with abundance increasing with time, as more complex species are destroyed by ion–molecule reactions. Hot-core models²² have also indicated that gas-phase HCN should have a strong abundance peak at intermediate temperatures (around 40–60 K), corresponding to the release of molecules formed by the surface hydrogenation of CN. These and other models⁵⁹ also

suggest that HNCO is formed primarily as a destruction product of COMs in hot regions.

Some simple molecules are also predominantly observed in extended, colder emission from gas that has not yet experienced the sublimation of the majority of grain-surface ice mantles; recent observations⁸⁵ indicate low (~ 50 K) rotational temperatures for H_2CO , indicating that significant amounts of this molecule may desorb from the grains at low temperatures, commensurate with its relatively low binding energy. This work indicates that other simple organics follow the same trend. However, other observations toward low-mass cores have indicated a second temperature component⁸⁶ for formaldehyde of around 100 K, corresponding to the evaporation temperature of water ice—a result that has been reproduced in the models of Vasyunin and Herbst.²³

7. COMPLEX MOLECULES

7.1. Background

The majority of the molecules detected in the interstellar medium are complex organic molecules, i.e., those containing five or more atoms.² While simple grain-surface chemistry on interstellar ices was thought to produce small organics in cold clouds,⁷⁶ it was long assumed that COMs formed predominantly in the warmer regions of star formation through gas-phase chemistry dominated by ion–molecule reactions.^{25,87} This assumption was based on the fact that only single-atom addition reactions could occur on ice surfaces in cold, dense clouds, where the temperatures were too low for polyatomic species to be mobile in or on the ice. Chemical complexity was therefore limited by the small set of reactions that were plausible under such conditions, as explained in section 6. The simple ice species that formed in colder regions would be liberated into the gas phase in the warmer regions associated with star formation, where they were assumed to serve as the chemical precursors to COMs. The gas-phase ion–molecule chemistry invoked to explain the presence of COMs in warm star-forming regions was therefore treated separately from simple grain-surface chemistry in cold regions.

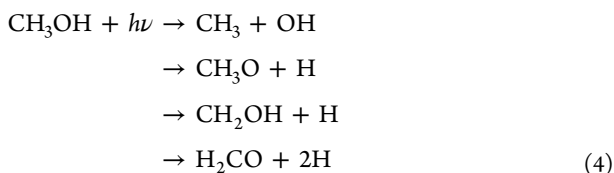
The separation of grain-surface and gas-phase chemistry limited the set of COMs that were predicted by astrochemical models, and it was therefore assumed that there was a limit to the level of chemical complexity that could be reached in interstellar environments. However, as observational capabilities advanced over the past decade, COMs began to be detected in regions where gas-phase reactions did not contribute significantly to chemical processing. For example, COMs such as dimethyl ether (CH_3OCH_3) and methyl formate (HCOOCH_3) were detected in cold clouds in the Galactic Center where grain mantles had been liberated by shocks.⁸⁸ Likewise, COMs such as methyl formate and acetic acid (HOCOCH_3) were detected in low-mass hot cores,⁸⁹ where the time scales for gas-phase processing are too short to explain the buildup of this level of chemical complexity through purely gas-phase formation mechanisms. Meanwhile, Horn et al.⁶⁵ conducted a detailed computational study of the formation of methyl formate, where they examined a series of ion–molecule reactions that had long been included in models of hot cores. This study revealed that the formation of methyl formate through gas-phase chemistry alone could not explain the observed abundances in hot-core regions. Additional laboratory studies of gas-phase reactions showed that many of the assumptions included in the models for the production of

COMs were not valid. The most significant finding here was in the examination of the protonated methanol (CH_3OH_2^+) electron recombination reaction, long assumed to be the primary path to gas-phase methanol and other smaller COMs in interstellar clouds. A CRYRING study by Geppert and co-workers³³ showed that this reaction predominantly leads to cleavage of the heavy atom bonds and that methanol comprises only ~3% of the products. These findings are particularly relevant for methyl formate, which had been previously proposed to form from gas-phase reaction of protonated methanol. This combined observational, computational, and laboratory evidence pointed to a grain-surface formation mechanism for methyl formate, and therefore potentially other COMs. It became clear that the existing models should be revised to account for these new observational and computational results.

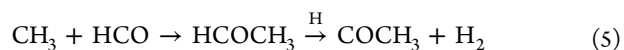
7.2. Gas–Grain Models of COM Chemistry

7.2.1. Chemical Models. Although complex grain-surface chemistry had been proposed,⁶⁵ this type of chemistry had not been incorporated into the standard gas–grain chemical codes maintained at OSU and UMIST. On the basis of the chemistry proposed by Allen,¹⁹ Garrod and Herbst⁶³ began to explore the possibility of grain-surface chemistry as a contributor to the formation of methyl formate and other COMs in star-forming regions and showed that methyl formate could be formed through grain-surface chemical mechanisms. Additionally, Garrod, Wakelam, and Herbst³¹ coupled the grain-surface and gas-phase chemical networks by addition of accretion and desorption mechanisms that relied on both thermal and nonthermal processes. The work of Garrod, Widicus Weaver, and Herbst²² provided a more comprehensive model examining COM chemistry in hot cores.

This model expanded upon the 2006 study⁶³ by incorporating photodissociation-induced radical–radical chemistry on ice surfaces during the warm-up phase of star formation. This approach assumed that simple ice molecules such as H_2O , CH_3OH , NH_3 , and H_2CO underwent direct and cosmic-ray-induced UV photodissociation to form small molecular radicals including OH, CH_3 , CH_3O , CH_2OH , NH_2 , and HCO. While these radicals are not mobile on ices at the 10 K temperatures of dense cores, they do become mobile at temperatures above 20 K. Therefore, these radicals can move and react from temperatures of ~20 to 100 K, above which the ice mantles are liberated into the gas phase. Simple combination reactions between the radicals on the ice surface build up a series of COMs, and subsequent hydrogen-abstraction reactions followed by further radical–radical combination reactions increase the level of complexity that is achieved. As an example, methanol photodissociation proceeds through the following reactions:



The radical products of this photodissociation reaction can then go on to react with other radicals on the ice surface to produce more complex molecules. For example, reaction with the HCO radical leads to methyl formate (HCOOCH_3) and its structural isomers acetic acid (HOCOCH_3) and glycolaldehyde (HOCH_2CHO) through the following sequence of reactions:



Even more complex chemistry can build up from subsequent reactions of molecules containing an aldehyde group, where the terminal hydrogen on the aldehyde is abstracted by a radical species. Additional radical–radical reactions can then occur between the remaining organic radical species and other radicals on the grain surface. The combination of reactions 5 and 6 above gives an example of this type of chemistry. A significant amount of chemical complexity can be built up through these simple surface addition and abstraction reactions.

Although the COM chemistry that is built up on the ice surfaces does reach a high level of complexity during the warm-up phase of star formation in these models, additional reactions involving gas-phase species can build up more chemical complexity during the hot-core phase. The chemical networks include protonation reactions for all COMs predicted to form on the grain surface, as well as reactions between the resultant ions and those neutral species that have dipole moments. Large, protonated COMs are formed by this type of chemistry. The products of these ion–molecule reactions then undergo electron recombination reactions, leading to the neutral parent molecule, as well as fragmentation reactions that lead to smaller organics.

7.2.2. Grain Temperature. The key to inclusion of COM grain-surface chemistry in astrochemical models is the incorporation of a temperature warm-up phase into the physical model assumed for the star-formation process. As outlined in section 5, led by the work of Viti and co-workers,²⁹ recent models have adopted a second-order power law for the temperature of the cloud profile (for both dust and gas) as it progresses from a prestellar core to a hot core/corino. A gradual rise in temperature enables radical mobility on the ice surface while delaying full ice-mantle liberation to the gas phase until higher temperatures, therefore offering suitable physical conditions to drive grain-surface chemistry. Such an effect cannot be achieved under static, or simple two-step, temperature conditions.

7.2.3. Results. The work of Garrod, Widicus Weaver, and Herbst^{22,63} and Laas et al.⁶⁴ incorporated the full gas–grain chemical model and the warm-up physical model to investigate hot-core chemistry. These studies were the first that gave plausible chemical pathways to the formation of methyl formate and other COMs in hot cores, with abundance predictions that matched reasonably well with observations. A comparison between the results of these models and observations is given in section 9.2.

Subsequent laboratory studies of photodriven ice chemistry confirmed that a gas–grain chemical network is a plausible route to COM formation in hot cores. Methanol ices were shown experimentally by Öberg and co-workers to form COMs such as ethanol, acetaldehyde, methyl formate, dimethyl ether, and many others upon UV irradiation.⁷³ Additionally, Bennett, Kaiser, and co-workers^{90,91} conducted experimental studies of cosmic-ray-induced photodissociation in pure and mixed methanol ices using an electron gun for ice processing. This work shows that a similar degree of molecular complexity is reached by both the cosmic-ray-induced and direct photo-

processing. Despite this progress, much work remains to be done from both laboratory and computational perspectives to gain quantitative information for the photodissociation branching ratios and the reaction rates for the relevant ice processes. Nonetheless, the results of these models and subsequent confirmation of this type of chemistry through laboratory studies have effectively demonstrated that this type of chemistry is likely a major contributor to the formation of COMs in interstellar clouds.

7.3. Structural Isomers and Other Tests of Model Predictions

Given the direct link between the ice precursor molecules and the COM products that can be formed via the various photodissociation pathways, the gas–grain chemical network points to interesting test cases where the abundance ratios of a set of related COMs can be used to test a particular chemical mechanism. For example, as shown in eqs 4–8, methanol photodissociates to CH_3 , CH_3O , and CH_2OH radicals, which can then go on to form a series of COMs. Here, the three structural isomers of acetic acid, methyl formate, and glycolaldehyde are formed by eqs 6, 7, and 8, respectively. Laas et al.⁶⁴ explored this mechanism in more detail using the reaction network and physical model of Garrod, Widicus Weaver, and Herbst²² and confirmed that the relative abundances of these isomers in interstellar clouds do depend on the branching ratios for the methanol photodissociation mechanism. This work has stimulated new laboratory studies of the methanol photodissociation mechanism in ices⁷³ and the gas phase.⁹²

In some cases the relative abundances of structural isomers can also be used to examine the relative contributions of grain-surface versus gas-phase chemistry, such as in the case of dimethyl ether (CH_3OCH_3) and ethanol (HOCH_2CH_3).²² While both are predicted to form through a combination of grain-surface and gas-phase processes in interstellar environments, the dimethyl ether that is formed in ices is ejected into the gas phase at lower temperatures than ethanol. This gives a longer time scale for the gas-phase destruction of dimethyl ether through ion–molecule reactions, leading to a predicted higher abundance of ethanol than dimethyl ether in the hot-core phase. Similar comparisons can be made using other sets of molecules, such that key chemical reaction pathways can be determined through comparison of the models with observations.

There are many subtleties involved in modeling COM chemistry that go beyond the simple comparisons described above, and caution must be taken in interpreting model results. For example, the formation and destruction of dimethyl ether is a complicated process in hot cores that involves grain-surface and gas-phase formation and destruction routes. A combined laboratory and modeling study of dimethyl ether photodissociation by Peeters and co-workers²⁷ showed that dimethyl ether predominantly forms from gas-phase chemistry in hot cores. However, dimethyl ether has also been detected in cold clouds.^{93,94} Therefore, any comparison with ethanol in a hot core must also consider the ongoing formation of dimethyl ether from purely gas-phase mechanisms.

7.4. Homologues of Key Hot-Core Molecules

A $\lambda=3$ mm line survey of the Galactic Center hot-core source Sgr B2(N), presented by Belloche et al.,⁹⁵ identified the possible glycine precursor aminonitrile ($\text{H}_2\text{NCH}_2\text{CN}$). The continuation of that work⁴ also identified emission from

the two most complex organic molecules yet detected in a star-formation region: ethyl formate (HCOOC_2H_5) and *n*-propyl cyanide ($\text{C}_3\text{H}_7\text{CN}$), the larger homologues of the previously detected hot-core molecules methyl formate (discussed above) and ethyl cyanide ($\text{C}_2\text{H}_5\text{CN}$). The detection of these molecules and the determination of their abundances and excitation temperatures provided a unique opportunity to test the radical–radical reaction processes thought to be operating on grain surfaces. Building on the Garrod, Widicus Weaver, and Herbst²² model, Belloche et al.⁴ added new surface formation and destruction mechanisms to the chemical network for the above-mentioned molecules. Similarly to the other reaction schemes, the larger molecules were allowed to form by the addition of HCO or methyl radicals to the hydrogen-abstraction products of previously formed COMs. In the case of ethyl formate, the photodissociation of methyl formate or ethanol could produce the required radicals. However, *n*-propyl cyanide also provided the possibility for formation via the addition of ethyl or propyl radicals to other radicals on the grains, as well as the possible hydrogenation of unsaturated molecules derived from gas-phase chemistry and accreted onto the dust grains.

Using the detected gas-phase abundances of the three alkyl cyanides identified toward Sgr B2(N)—methyl, ethyl, and *n*-propyl cyanide—along with that of aminonitrile, the grain-surface production mechanisms could be tuned to match observed values. The only reaction scheme that could reproduce the relative abundances of each species was that in which the majority of each of the alkyl cyanide homologues was formed by the sequential photodissociation of the smaller molecule, followed by the addition of a methyl radical. Mechanisms allowing the efficient formation of ethyl or *n*-propyl cyanide that involved ethyl or propyl radical addition were ruled out, as was grain-surface hydrogenation of gas-phase-derived structures. In the case of both ethyl formate and *n*-propyl cyanide, the addition of methyl groups was found to be the dominant formation route. It is indeed plausible that similar methyl addition routes apply also to other classes of molecule detected toward hot cores.

Thus, the detection and chemical modeling of homologues in star-formation regions provides a valuable means to tune key model parameters and identify the dominant chemical mechanisms on the grains.

7.5. Laboratory and Modeling Studies of Ice Processing

The addition of this type of grain-surface chemistry to the standard gas–grain chemical network has led to numerous studies that explore the details of this type of chemistry from both modeling and laboratory perspectives. As mentioned above, the UV processing of methanol ices conducted by Öberg and co-workers⁷³ showed that COMs can be readily formed under conditions relevant to the warm-up phase of hot cores. This study incorporated a model that examined the reaction network within the ice on the basis of the specific ice composition used for the laboratory experiment. This study demonstrated that the grain-surface reaction network assumed in the gas–grain hot-core model²² used a reasonable set of reactions to model this type of chemistry. Bennett et al.⁹⁰ confirmed through laboratory studies of methanol ices that cosmic-ray-induced photodissociation is also efficient for COM production. Additional studies by Modica and Palumbo³⁵ showed that direct cosmic-ray-induced processing of ices can produce COMs in methanol ices, even at very low temper-

atures. This study demonstrated that methyl formate can be formed at 10 K from the bombardment of methanol + CO ices with high-energy protons.

Recent modeling studies have further examined the methyl formate and glycolaldehyde formation mechanisms at low temperatures by adding to the list of possible reactions that can produce each species and providing limits as to the contributions of various grain-surface and gas-phase formation mechanisms at 10 K.^{34,36} These studies show that the grain-surface reactions assumed in the gas–grain model²² are only efficient at the warmer temperatures associated with star formation, but that there are other surface processes that may contribute to COM formation at lower temperatures. For example, cosmic ion irradiation of CO followed by reaction with methanol has been shown as a viable route to produce the observed quantities of methyl formate in dark clouds.³⁴ However, this study showed that the radical–radical reactions included in the gas–grain networks must be invoked to explain the abundances of methyl formate in warmer regions of star formation. These studies indicate that the chemical network included in the gas–grain code should be expanded to include more COM formation mechanisms that are efficient at low temperatures. However, given the limited number of COMs that have been studied, more laboratory work needs to be done to fully investigate the role of ice processing at low temperatures before such chemistry can be added to the gas–grain reaction networks.

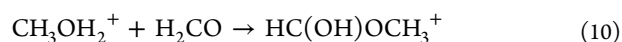
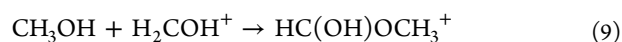
There is recent observational evidence that supports the laboratory and modeling findings and suggests that lower temperature formation mechanisms for COMs may be possible. Bacmann and co-workers⁹³ have detected methyl formate, acetaldehyde, dimethyl ether, and ketene in the L1689B prestellar core. This particular region has not undergone shocks, nor has it begun the warm-up phase associated with star formation. At the cold temperatures of this core (11–12 K), the radical–radical addition reactions, such as the ones assumed in the gas–grain chemical networks,²² are not efficient formation routes for COMs. These authors suggest that radicals in the ices may become mobile through nonthermal processes, possibly including processing by secondary UV photons, cosmic rays, or energy released from exothermic reactions. Other recent studies have reported detection of COMs released from UV processing of icy dust grains in the cold core associated with the B1-b source,^{94,96} in the envelopes around several low-mass embedded protostars in the Serpens core,⁹⁷ and in the L1157-B1 molecular outflow.⁹⁸ On the basis of these findings, additional investigation of other physical or chemical processes that may contribute to COM formation in young protostars is warranted.

It should be borne in mind that the fluxes adopted in laboratory experiments are necessarily much higher, and time scales commensurately shorter, than in interstellar environments. Experimental UV fluxes⁷³ of $\sim 10^{13}$ photons $\text{cm}^{-2} \text{s}^{-1}$ may be compared with the unattenuated interstellar UV field⁹⁹ of $\sim 10^9$ photons $\text{cm}^{-2} \text{s}^{-1}$, or the cosmic-ray-induced UV field appropriate to the interiors of dense cores¹⁰⁰ (and, indeed, hot cores, protostellar radiation notwithstanding) of $\sim 10^4$ photons $\text{cm}^{-2} \text{s}^{-1}$. While the experimental time-integrated fluxes (i.e., fluences) are typically chosen to match interstellar conditions, it is as yet unclear to what degree the elevated flux values may affect the qualitative behavior of the chemical kinetics within the ices; such must be dependent on the level of competition from nonphotonic processes in the ice, such as thermal

diffusion, and indeed on the influence of UV-induced excitation on diffusion rates. Greater knowledge of the precise mechanisms driving the complex chemistry within irradiated organic ices will aid in resolving this question.

7.6. Reconsideration of Gas-Phase Chemistry

In addition to the grain-surface chemistry additions to astrochemical models, new gas-phase mechanisms for the production of COMs have also been considered. Laas et al.⁶⁴ examined other possible ion–molecule formation pathways for methyl formate that were not included in the Horn et al.⁶⁵ study. Here, the Fischer esterification reaction between methanol and protonated formaldehyde (shown in eq 9) and the methyl cation transfer reaction between formaldehyde and protonated methanol (shown in eq 10) were both considered.



Stereochemistry becomes an important consideration here. The *cis* isomer of methyl formate is the lower energy isomer and is the one that is routinely observed in interstellar clouds. The *trans* isomer of methyl formate is considerably higher in energy, and there was no spectroscopic information available for this isomer before these reactions were considered. Both reactions given in eqs 9 and 10 proceed through high-barrier pathways to form the *cis* isomer of protonated methyl formate, and these barriers minimize the possible contributions from these pathways to the gas-phase production of methyl formate. However, the reaction given in eq 7 proceeds through a barrierless pathway to form the *trans* isomer of protonated methyl formate. This ion can then form neutral *trans*-methyl formate via electron recombination reactions. These reactions were incorporated into the gas–grain code of Garrod, Widicus Weaver, and Herbst,²² and modeling studies showed that significant amounts of *trans*-methyl formate can be formed in a hot core via this reaction pathway.⁶⁴ Subsequent observational studies reveal a tentative detection of *trans*-methyl formate in the Orion hot core.⁶⁸ This is the first modeling study⁶⁴ to consider the effects of stereoisomerism in COM chemistry; it is possible that there are other previously uninvestigated pathways that involve higher energy stereoisomers of known interstellar molecules that can significantly contribute to the formation of COMs in hot cores. Additional observational searches to investigate the protonated precursors to such molecules (i.e., protonated methanol, protonated formaldehyde, etc.) and the higher energy isomers would be quite helpful, but are limited by the lack of laboratory spectral information for these species.

7.7. Effects of Warm-Up Time Scales for Hot-Core Models

In addition to these chemical studies, the addition of a warm-up phase to the physical model of star formation used in the aforementioned modeling studies^{22,63,64} has enabled comparison of the chemical complexity reached in the hot-core phase of various masses of young stellar objects. Garrod, Widicus Weaver, and Herbst²² varied the warm-up time scales to investigate the relative COM abundances in low-, intermediate-, and high-mass hot cores. Simulations were conducted with fast, medium, and slow warm-up time scales of 5×10^4 , 2×10^5 , and 1×10^6 years, respectively. However, the results of this work must be carefully interpreted, as there is some discrepancy in the literature as to whether low-mass star formation is more or less rapid than high-mass star formation. Viti and co-workers²⁹ propose that the star-formation rate is dependent on the size of

the object, with shorter time scales corresponding to high-mass star formation and longer time scales corresponding to low-mass star formation. However, Aikawa and co-workers¹⁰¹ propose that the warm-up time scale is related to the ratio of the size of the hot core to the infall speed, rather than the overall speed of star formation. The results of the gas–grain model²² indicate that some of the complex species observed in low-mass hot cores may require longer warm-up time scales in the 10–50 K temperature range, where COMs are efficiently formed on grain surfaces, and shorter time scales in the 50–100 K temperature range, where some of the COMs are readily destroyed through secondary grain-surface reactions. These results indicate that the warm-up time scales proposed by Aikawa and co-workers¹⁰¹ may be most appropriate for low-mass hot cores.

Figure 4 shows time- and temperature-dependent fractional abundances (with respect to total gas density) for the three warm-up time scales modeled by Garrod, Widicus Weaver, and Herbst,²² using the recent three-phase chemical model of Garrod.⁴² The main sublimation phase may be seen to occur a little above 100 K in each case, at which temperature both water and methanol desorb rapidly. The slower warm-up models naturally correspond to longer periods of destruction of gas-phase COMs, following their sublimation. The destruction rates are not vastly different in each case, but the period of time spent at any particular temperature is longer, resulting in lower abundances of COMs at high temperatures for the slower warm-up models. Methanol abundance falls over time, as it is used up to form both simpler molecules in the gas phase and—in the case of dimethyl ether (DME)—a more complex one. The reaction between methanol and protonated methanol leads to the formation of a significant quantity of DME, in spite of the inefficiency of dissociative recombination (see sections 4.2 and 7.1). This mechanism is seen to be the dominant source of DME at high temperatures. DME is formed in abundance on the grains at warm (~ 20 –40 K) temperatures, but sublimates relatively early, before the majority of other species, leaving it susceptible to rapid destruction by ion–molecule reactions. For the longer time scale models, this means that the early peak is much lower than the later gas-phase peak. Formaldehyde may also be seen to have two peaks in its abundance, one resulting from its sublimation at around 40 K and the other due to gas-phase destruction of other molecules at higher temperatures. Grain-surface formation of methyl formate is seen to be sufficient to produce appropriate gas-phase abundances following its sublimation at around 100 K. Its sublimation occurs slightly earlier than that of water and most other COMs, such that, in the slow warm-up model, there is an appreciable falloff in abundance as described for DME.

It may also be noted that, for the slowest warm-up period, there is an appreciable degree of destruction of grain-surface molecules prior to their sublimation. This is because these surface-bound COMs are still subject to photodissociation and destruction by chemical reaction, while their optimal temperatures of formation have already passed and/or the simpler molecules from which they most easily form have already sublimated.

7.8. Contributions from Bulk-Ice Chemistry

There is experimental evidence that suggests that bulk-ice processes could also be important contributors to COM formation in interstellar clouds in addition to the surface chemistry. The experiments of Öberg and co-workers⁷³

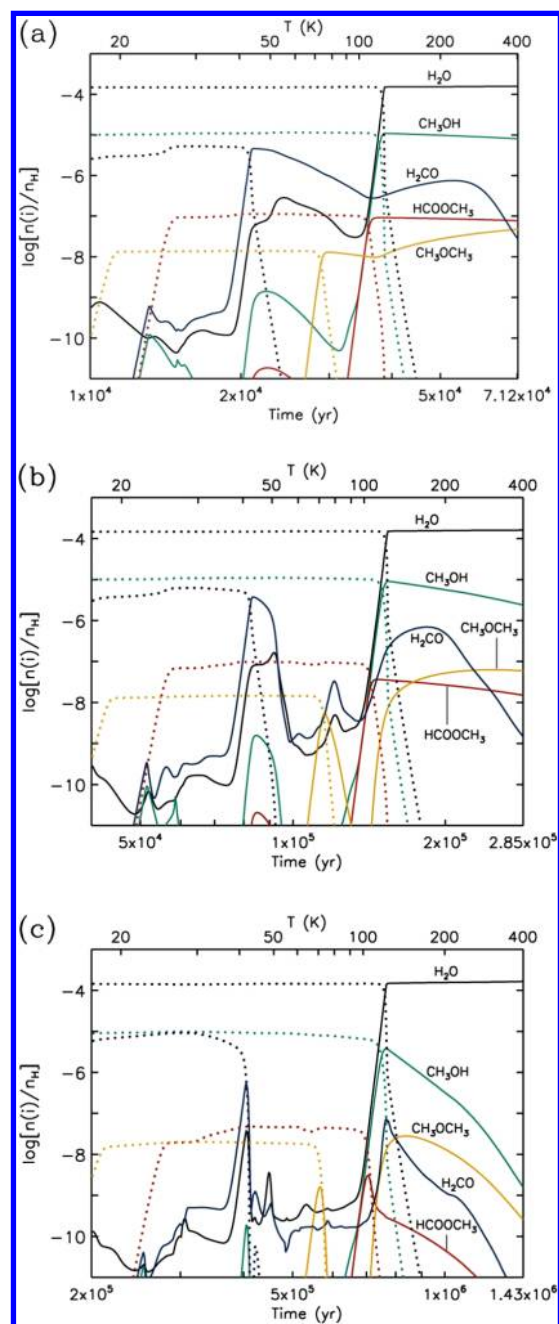


Figure 4. Simulated time-dependent abundances with respect to total hydrogen (n_{H}) of a selection of abundant and/or complex molecules during the warm-up phase of hot-core evolution. Results were taken from the Garrod⁴² model, which includes a fully active ice mantle and surface chemistry. Panels a–c show the results for fast, medium, and slow warm-up periods, respectively; temperatures, indicated on the upper axis, follow a quadratic time dependence. Solid lines indicate gas-phase species, while dotted lines of the same color represent the same species in the solid phase. Data were derived from ref 42.

investigating photoprocessing of methanol ices showed that surface reactions were at most twice as efficient at producing COMs than were reactions in the bulk ice. Additional experiments from Öberg and co-workers⁵⁰ show that segregation is important in $\text{H}_2\text{O}/\text{CO}$ and $\text{H}_2\text{O}/\text{CO}_2$ ice mixtures, where surface diffusion dominates the segregation rates in thin ices (8–37 ML) and bulk diffusion dominates the segregation rates in thick ices (>100 ML). Building on these

studies, recent work from Fayolle et al.¹⁰² couples laboratory experiments investigating H₂O/CO₂ ice desorption with a three-phase model that includes gas, ice-surface, and bulk-ice-mantle processes. They find that the desorption process is a complicated scheme where some molecules remain trapped in the bulk ice, but that the amount of species trapped in the ice depends on the ice composition, ice mixture, and ice thickness.

Modeling bulk-ice processes that are relevant to COMs presents a challenge to current approaches for several reasons: the precise mechanism for the bulk diffusion inferred from experiment has not been specifically identified, making parametrization of the temperature-dependent diffusion rates difficult; bulk-ice processes may in some cases involve much more complicated, multistep chemical mechanisms, perhaps with photoexcitation playing a role; and the chemical segregation of portions of the bulk ice may require at least a nominal treatment of layering when treating chemistry within the bulk ices. However, it should be noted that rate-equation-based models such as that of Garrod, Wicnicus Weaver, and Herbst²² adopt a de facto bulk-ice chemistry, albeit governed by surface chemical parameters (see section 7.2).

Microscopic Monte Carlo simulations^{43,72,77} of surface processes have been successful for very simple systems with limited chemistry as described above. One such study by Cuppen and co-workers¹⁰³ considered methanol and formaldehyde formation through ice-surface hydrogenation reactions, but this work did not extend to more complex chemistry because including more chemical complexity or bulk processes is computationally challenging.

The unified Monte Carlo hot-core chemical model of Vasyunin and Herbst,²³ discussed in section 3.2.4, coupled a multilayer bulk-ice model with gas-phase and grain-surface chemistry, assuming an inert bulk-ice mantle. Upon the warm-up of the hot core, the bulk-ice material is cycled back through the ice surface layer in the order in which it was deposited, allowing elements of the trapping behavior observed in mixed-ice desorption experiments to be reproduced.

The three-phase approach has been extended in another direction by Garrod⁴² to incorporate a fully active bulk-ice chemistry using the modified-rate approach, with a reaction network similar to that used for the ice surface, building on previous networks.^{4,22,63,64} The bulk-ice population is representative of the ice mantle as a whole and is not segregated into separate layers; however, the inclusion of bulk diffusion allows more mobile species to migrate within the ice, including into the surface layer. This approach results in complex interactions between the surface and bulk-ice chemistry, which are quantitatively different; the surface chemistry is more directly dependent on gas-phase–surface interactions, and the chemistry is dominated by more volatile species, while bulk processes are slower and the loss of volatiles to the surface with increasing temperature lends a slight bias toward more complex molecules. It is clear that the hot-core models of Vasyunin and Herbst²³ and Garrod⁴² take very different approaches, while aiming to resolve different challenges in the simulation of hot-core ice chemistry and structure.

7.9. Desorption Processes and Chemistry in Evaporating Ices

Coupled with the challenge of modeling bulk-ice processes is the consideration of the ice desorption mechanism and possible chemistry that could occur during evaporation. Early chemical models assumed an instantaneous temperature jump and were

not concerned with complicated desorption mechanisms, instead relying on the assumption that all ice components were ejected into the gas phase simultaneously. However, the experimental study of Collings and co-workers³⁰ showed that the desorption processes for ice species are highly temperature dependent. This study also showed that a single desorption mechanism can be attributed to a group of molecules with similar binding properties in water ice, rather than for each molecule individually. For example, molecules that undergo hydrogen bonding within water ice follow the desorption behavior of water, while less polar molecules such as methane, O₂, N₂, and NO follow the desorption behavior of CO. On this basis, the water-like species can be assumed to codesorb with the water ice during the warm-up phase of star formation, while the less polar CO-like species undergo much more complicated desorption mechanisms that involve monolayer desorption at surfaces, multilayer desorption in the bulk ice, and volcano desorption for trapped species. The warm-up model introduced by Viti and co-workers²⁹ incorporated these findings into a hot-core model, where the gradual warm-up allowed for these varying desorption mechanisms. The model demonstrated a commensurate discretization of chemical events in the gas phase as a result of the release of each set of molecular ice species.

Building on these earlier studies, the desorption models for various ices have become more sophisticated as laboratory measurements have advanced. The most recent study of desorption rates of pure ices by Brown and Bolina¹⁰⁴ included a model that calculated molecular residence times for water, methanol, and ammonia in astrophysical environments. A similar study by Noble et al.¹⁰⁵ examined formaldehyde desorption. Despite this progress in understanding the desorption mechanisms for the major constituents of interstellar ices, much work remains to be done to fully understand complex ice mixtures that are more directly comparable to interstellar ices. The work of Öberg et al.⁵⁰ examined mixtures of water ice with CO₂ and CO, but focused on ice segregation, while the subsequent study of Fayolle et al.¹⁰² examined volatile entrapment processes in the bulk ice for similar ice mixtures.

A recent study by Cecchi-Pestellini et al.¹⁰⁶ investigated the possibility of gas-phase chemistry occurring during the desorption process. In this study, they treated the species desorbing from the ice as a high-density plume of gas adiabatically expanding into lower density. As this plume expands, the ejected molecules have a much higher collision frequency than the typical interstellar gas molecule, and therefore can undergo more rapid gas-phase reactions than are typically observed in dense clouds. This study takes a preliminary look at the possibility for complex chemistry through this mechanism, considering only a small number of molecules, and applying the mechanism more broadly only for a model where no specific molecules were considered. Instead, probabilities of collisions between pairs of reaction partners were considered. The lack of specific chemical reactions means that the results of this study are highly speculative at this time, and more extensive studies that include specific interstellar molecules need to be conducted.

8. BIOLOGICALLY RELEVANT MOLECULES

One of the great motivations for studying COMs in star-forming regions is to trace potential chemical pathways to the formation of biologically important molecules. Some fraction of

the COMs that form in these regions will be incorporated into the condensed material of the new solar system. Therefore, interstellar COMs have the potential of serving as the precursors to larger biomolecules that could ultimately lead to the formation of life. Of particular importance in interstellar studies are the simplest versions of key biomolecules, including sugars, amino acids, and nucleobases. Here, modeling work has focused on the simplest sugar-related species glycolaldehyde (HCOCH_2OH), as well as the simplest amino acid, glycine ($\text{H}_2\text{NCH}_2\text{COOH}$).

8.1. Glycolaldehyde

Glycolaldehyde is an α -hydroxy aldehyde that has the general empirical formula for a sugar, $\text{C}_n\text{O}_n\text{H}_{2n}$. The standard definition of a sugar includes that it be a polyhydroxylated species; therefore, glycolaldehyde is not technically a sugar because it contains only one $-\text{OH}$ moiety. However, given that its empirical formula and chemical behavior match those of sugars, it is often grouped into this same chemical category. Glycolaldehyde has been detected in several star-forming regions, including Sgr B2(N),^{107–109} G31.41+0.31,¹¹⁰ and IRAS 16293-2422,¹¹¹ and tentatively detected in G24.78+0.08.¹¹² Glycolaldehyde was found to be much less abundant than its structural isomers methyl formate and acetic acid in the Sgr B2(N) hot core, and this discovery led to several modeling studies that have attempted to explain its low abundance. The papers dealing with the observational detection of glycolaldehyde offer only limited explanation for its production. In the original detection paper by Hollis et al.,¹⁰⁷ the authors state, “There is no theoretical formation mechanism for either gas-phase chemistry or grain-surface reactions that accounts for interstellar glycolaldehyde.” The work of Beltrán et al.¹¹⁰ does mention possible production pathways from HCO , H_2CO , and CH_3OH on grain surfaces, but the authors go on to state that “these somewhat arbitrary choices do not imply that other routes are not important”. Neither of these detection studies claim a definitive model for glycolaldehyde formation. However, the grain-surface chemical network proposed by Garrod, Widicus Weaver, and Herbst²² was partially motivated to explain the varied abundances of glycolaldehyde and its structural isomers. While this work did provide plausible pathways to the formation of these molecules through photodriven grain-surface chemistry, this study did not fully explain the observed abundances in Sgr B2(N). The follow-up study conducted by Laas et al.⁶⁴ built on this previous work and focused specifically on these three structural isomers. It was found that changing the photodissociation branching ratios for methanol on the ice surface could explain the varied abundance ratios of glycolaldehyde, methyl formate, and acetic acid. However, the abundance of glycolaldehyde predicted by this model for the warmest regions of the hot core is much higher than observed in any source, indicating that some gas-phase destruction mechanism(s) for glycolaldehyde may be missing from the gas–grain chemical networks.

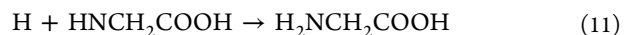
Alternatively, Garrod⁴² suggested that the reaction of HCO and CH_2OH radicals to form glycolaldehyde on dust grains may be inefficient, with an alternative branch producing $\text{CO} + \text{CH}_3\text{OH}$ as the favored outcome. However, the efficiency of this and similar processes in the solid phase has not yet been determined experimentally or computationally, and similarly to the estimates of activation energy barrier parameters, measured gas-phase values may provide a poor representation of the solid-phase process.

The recent study of Woods et al.³⁶ explores other options for glycolaldehyde formation that go beyond the simple radical–radical addition reactions proposed for the grain-surface chemistry. In this work, the authors investigate five reaction mechanisms that have been proposed in the literature for glycolaldehyde formation to assess the likelihood that this molecule can be formed at the low temperatures of a cold core. They find that while the radical–radical reactions are efficient for warmer regions of star formation, at 10 K, two other grain-surface mechanisms are more plausible formation pathways for glycolaldehyde in colder regions. The first involves the direct reaction of CH_3OH with HCO ; the second involves the reaction of H_3CO and HCO . Further observational studies that provide limits on glycolaldehyde abundances in cold cores, as well as more quantitative reaction rate determinations, are required to further constrain this problem.

8.2. Glycine

The simplest amino acid, glycine ($\text{H}_2\text{NCH}_2\text{COOH}$), has long been the target of interstellar searches,^{113–116} and although it has yet to be positively identified in interstellar spectra,¹¹⁷ glycine has indeed been detected in meteorites and has been identified¹¹⁸ in samples taken from the comet *Wild 2*. This, combined with the detection of molecules similar to glycine in hot cores, such as acetic acid¹¹⁹ and aminoacetonitrile⁹⁵ ($\text{H}_2\text{NCH}_2\text{CN}$), both likely formed on dust grains, gives reason to consider whether glycine may also be present in some significant abundance. The question becomes yet more relevant with the availability of high spatial and spectral resolution with the ALMA telescope over the coming years.

Garrod⁴² specifically addresses this question, using a three-phase chemical model with active ice-mantle chemistry (described in section 7.8), applying the results to a radiative transfer model to make predictions about the strength of putative glycine emission lines in a nearby hot-core source. The chemical network used in this study adopts four radical–radical formation mechanisms for glycine in the surface/bulk-ice chemical network:



The first of these processes is of minor importance, occurring mainly as the result of hydrogen abstraction from glycine itself. The three latter reactions require prior hydrogen abstraction either from detected complex species such as formic acid (HCOOH), acetic acid (CH_3COOH), or methylamine (NH_2CH_3) or from glycinol ($\text{H}_2\text{NCH}_2\text{CHO}$), the amino aldehyde corresponding to glycine, for which other formation routes are also included. In fact, each of the three reactions contributes significantly to glycine formation on the grains, while the precise balance is determined by the warm-up time scale of the hot core. The peak abundances achieved in the model fall in the $\sim 10^{-10}$ – 10^{-8} range with respect to hydrogen, in line with a large range of observed COM abundances. However, crucially, the evaporation of the solid-phase glycine into the gas phase occurs at ~ 400 K in this model, a temperature which is achieved only in very compact regions of the hot core; this would indicate that previous nondetections of glycine were caused by the lack of spatial resolution in the

observations. The mapping of the model results onto a combined temperature–density–radius profile obtained from dust observations⁷⁸ for the hot-core source NGC 6334 IRS1 indicate that glycine may be detectable in bright, nearby sources with narrow emission lines, assuming that glycine emission is not strongly blended with emission from other molecules. The results are also consistent with the current nondetection of glycine.

Another important finding of this model was that the photodissociation of the large quantities of water and ammonia in the granular ices may be responsible for the production of the majority of molecular radicals above temperatures around 40 K. The OH radical may be sufficiently mobile in this regime to abstract hydrogen atoms from complex molecules, including methanol; similar effects may also occur as a result of hydrogen abstraction by NH₂ radicals formed by abstraction from ammonia by mobile OH radicals. However, such effects must be confirmed through laboratory study, and the specificity of these processes will be strongly dependent on the relative rates of abstraction and OH/NH₂ diffusion in the ices.

9. INTERPRETATION OF MODELS AND COMPARISON WITH OBSERVATIONS

9.1. Uncertainties in Models and Observations

Full interpretation of astrochemical models requires the direct comparison of results with observational data sets. In some cases, the simulation included in a given model may directly incorporate the information obtained through observations. There are challenges that arise when making such comparisons because of the semi-quantitative nature of the information included in the models as well as the inherent uncertainties associated with the observations. In terms of the models, many of the parameters included in both the reaction networks and the physical models are estimated or calculated, rather than directly measured. Uncertain chemical parameters include, but are not limited to, branching ratios, dipole moments, binding energies, and reaction enthalpies, all of which influence the reaction rate coefficients that are included in the chemical network. Likewise, many physical parameters that are assumed for the model—including temperatures, densities, size scales, cloud homogeneity, and the time dependence of each of these parameters—have significant uncertainties.

Although the observations are often better constrained than the models, there are also some inherent uncertainties associated with the observational measurements that can lead to challenges in comparing models and observational results. Snyder and co-workers¹¹⁷ overviewed the challenges faced when analyzing observational data to determine molecular abundances and temperatures. Many molecular observations rely upon spectral analysis, but the spectra often have no associated imaging information; the derived molecular column densities are therefore not scaled appropriately to account for the spatial resolution of the telescope as compared to the source size. Additionally, spectral intensity calibration is often challenging; this is especially true when the common chopper-wheel calibration method is used, which yields spectral line intensity uncertainties of >7%.¹²⁰ Spectral line confusion from deep integrations and incomplete spectral catalogs for COMs also lead to difficulties in full spectral modeling, which results in uncertainties when determining physical parameters through spectral analysis. Added to these challenges is the limitation of observational data sets, where often only a handful of sources

are available for comparison to the models. While the physical model that is chosen for a given comparison can be fine-tuned to the particular source that is being considered, it is often the case that the model results are not then transferrable to studies of other sources.

The uncertainties associated with both the astrochemical models and the observations have led to new work in each area that attempts to quantify the necessary parameters and better constrain their uncertainties. Comprehensive efforts are now under way by Wakelam and co-workers⁶⁷ to evaluate and update the values of reaction rate coefficients used in models and their associated uncertainties, with particular emphasis placed on those reactions that are shown to be dominant chemical pathways in gas–grain chemical models. This analysis is stimulating additional laboratory work in several groups to measure rate coefficients for these important reactions. In terms of observations, the advent of new broad-band spectral capabilities and higher sensitivity is increasing the number of sources observed and the amount of frequency coverage obtained for these sources. There are several ongoing collaborative efforts to conduct broad-band line surveys on a number of rich molecular sources, including, but not limited to, the HEXOS¹²¹ and CHESS¹²² key programs using the Herschel Space Observatory. The ALMA observatory has also begun science observations, and the spatial resolution and frequency coverage offered by this observatory will continue to increase during its commissioning. This telescope will soon begin providing the detailed observational information needed for full spectral analysis and comparison to models.

9.2. Comparison of Hot-Core Models to Observations

Despite the uncertainties listed above, it is still possible to make semi-quantitative comparisons between modeling and observational results. Given the fundamental role of ice chemistry in the complex chemistry of a hot core, it is important to begin any hot-core simulation with realistic ice abundances. Comparisons must be made between model results for the cloud collapse phase to ice observations in YSOs so that the best set of initial conditions can be used in the hot-core simulation. Table 1 gives the typical ice compositions toward low-mass and high-mass protostars and background stars as determined from Spitzer observations,²¹ compared to the gas–grain model²² and Monte Carlo model²³ results for the cloud collapse phase that best match observations. The Monte Carlo simulation overpredicts the abundance of CO and CO₂ in the ice mantles, while the rate equation approach underpredicts these values. Both models match well with observations on the CH₃OH and CH₄ abundances, but severely overpredict the NH₃ abundance compared to observations. This overprediction of NH₃ may have serious implications for the COM chemistry predicted by the hot-core model, as reactions of NH₃ photodissociation products compete with the reactions involving CH₃OH photodissociation products, which can lead to significantly lower abundances of some COMs.

Similar comparisons can be made between the hot-core simulations and gas-phase column densities determined from observations. Garrod, Widicus Weaver, and Herbst²² provide an extensive list of predicted abundances for COMs and compare them to the observational results in the Sgr B2(N) source. They compare the peak gas-phase abundances for a given molecule predicted by the model and consider several time scales for the warm-up phase of the hot core. The results for the slow and fast warm-up time scales for a few key COMs are

Table 4. Molecular Abundances (cm^{-2}) for a Set of Complex Organic Molecules in Several Sources, Compared to the Peak Gas-Phase Values Predicted by the Gas–Grain Model in Ref 22^a

molecule	source ^{22,85,86,89,96,98,111,123}							model ²²	
	B1-b	IRAS 16293-2422	NGC 1333 IRAS 4A	G75.78	W3(H ₂ O)	W 33A	Sgr B2(N)	slow warm-up	fast warm-up
CH ₃ OH (warm)		2.0E+16		1.10E+17	1.00E+18	2.00E+17	2.49E+18	4.20E+18	9.60E+18
CH ₃ OH (cold)	3.60E+14	8.1E+14	5.1E+14				5.10E+15	3.30E+15	9.60E+14
HCOOCH ₃	4.40E+12	1.3E+16	5E+16	7.10E+15	5.20E+16	2.50E+16	5.70E+16	1.35E+15	2.34E+14
CH ₃ OCH ₃	3.0E+12	1.5E+16	<4.5E+16	2.30E+16	1.50E+17	2.70E+16	3.90E+15	1.26E+16	9.00E+15
CH ₃ CHO	2.80E+12	2.4E+15		<2.1E+13	3.50E+13	<3.0E+13	2.19E+14	1.14E+15	8.40E+12
HCOCH ₂ OH	<0.41E+13	4.0E+16						1.74E+14	2.64E+14
CH ₃ CH ₂ OH	<0.48E+13			<2.4E+15	5.70E+15	8.40E+15	4.70E+15	4.50E+16	4.50E+15

^aModel results from both fast (5×10^4 years) and slow (1×10^6 years) warm-up time scales are included for comparison.

presented in Table 4 and compared to observational results as presented in this same study, as well as results from two other observational studies that include both low-mass and high-mass hot cores.

The information presented in Table 4 reveals interesting trends in the modeling results that can be used to guide future modeling studies. Reasonable agreement between the model prediction and observations is found, with the predicted column densities for most of the COMs included here matching observations to within an order of magnitude. Specifically, the predicted column densities for the warm component of methanol match well with high-mass hot cores such as Sgr B2(N) and W3 (H₂O), regardless of the warm-up time scale. Likewise, the column densities predicted for the cold component of methanol match well with those observed in the prestellar core B1-b and in the extended envelope of the Sgr B2(N) cloud.

In the case of more complex species, the fast warm-up time scale leads to lower peak abundances for most COMs, as the amount of time available for grain-surface formation is less. Conversely, the longer period spent by the slow warm-up model in the important 20–40 K range maximizes complex molecule formation.

The low-mass hot cores IRAS 16293-2422 and NGC 1333 IRAS 4A show excellent agreement with the slow warm-up time scale model for the COMs, but do not display a good match for simpler species. In most cases listed here, it is the slow warm-up time scale model that best matches with observations, even when comparing to a high-mass hot core such as Sgr B2(N) or W3 (H₂O).

These results show that there are reasonable matches made for particular molecules if particular warm-up time scales and temperatures are considered. However, there is not one physical model listed here that agrees well with all species in a given source. It is therefore dangerous to draw comprehensive conclusions from these reasonable agreements between models and observations. Likewise, it should be noted that, for all values in Table 4, the column densities have been scaled to account for beam dilution on the basis of the source size and the telescope beam size. This step is crucial before comparisons with models can be made, and yet is not always included in the analysis of observational data sets because imaging studies are often not available. Complicating this matter further are the findings of recent observational studies of COMs in Orion-KL by Favre et al.,¹²⁴ Neill et al.,⁶⁸ and Widicus Weaver and Friedel,¹²⁵ which demonstrated that not all COMs in a given source follow the same spatial distribution. This presents a

challenge for modeling studies, where most physical models assume that all molecules occupy the same parcel of gas. Neill et al. suggest that chemical processes may shape spatial distributions of molecules in interstellar clouds. Friedel and Widicus Weaver¹²⁶ also show evidence that some molecular spatial distributions are correlated with physical conditions, in this case specifically temperature. While Orion-KL is an extreme case of complicated star formation, these results demonstrate that in some cases the gas–grain codes involving single-point calculations as a function of physical parameters are no longer sufficient for simulations of physical environments with complex morphology. Hydrodynamic models that incorporate complex chemistry are the crucial—and challenging—next step in simulations of hot-core chemistry. Such studies are challenging because the combination of an extensive chemical network with a sophisticated hydrodynamic model is computationally demanding. Additionally, any such study must be guided by high-resolution imaging studies of each molecule of interest, which is a significant time investment of observational facilities. Fortunately, such information is forthcoming as the ALMA observatory begins routine science observations with broad-band spectral coverage and high spatial resolution. A more detailed discussion of hydrodynamic modeling studies is explored elsewhere in this issue.¹²⁷

9.3. Spectroscopic Models

As mentioned above, there are inherent uncertainties involved in the comparison between fractional chemical abundances (with respect to hydrogen) calculated using single-point models and values derived from observed column densities for molecules along a line of sight. The varied physical conditions and dynamics—and the associated chemical variations—pertaining to hot cores, combined with observational limitations mean that *detailed* comparison with models will in the future require a more specialized approach. A more profitable comparison may perhaps be made by translating the chemical model results into emission spectra that may be compared directly with observed spectra. Such an approach requires knowledge of the spatial dependence of physical conditions within specific hot-core sources. A fully self-consistent approach would use these conditions to guide hydrodynamic models that could describe the physical evolution of the gas prior to its observed state, so that the modeled time-dependent chemistry could reflect all of these influences. While such approaches have advanced a great deal in the case of low-mass star formation,^{101,127–129} there is much uncertainty in the current understanding of the formation of high-mass protostars.

Nevertheless, the chemical model results may still be used in conjunction with physical profiles, post hoc, to produce spectroscopic simulations for well-defined sources, thereby avoiding the problematic comparison of fractional abundances with column-density-derived values. Garrod⁴² mapped the time- and temperature-dependent chemical abundances produced by a fixed (high)-density hot-core model to an observed temperature–density–radius profile for the source NGC 6334 IRS1 obtained from dust emission observations and modeling conducted by van der Tak.⁷⁸ The density function was combined with the resulting radius-dependent fractional abundances to construct a spherically symmetric abundance and temperature map for every species in the model. From these, the radiative transfer coefficients relating to the molecular emission could be calculated, and integrated along lines of sight, to be convolved to simulate telescope observations. This treatment proved effective in reproducing observed line intensities⁸⁵ for methanol and methyl formate, and predictions were made for putative glycine emission. Such methods may prove valuable as predictive tools for the structure of regions of emission for specific molecules, and for potential line blending in complex spectra, even where (as in most cases) the time dependence of the physical conditions is poorly defined. Future such spectroscopic simulations will, however, require much more detailed physical structure models, as ALMA reveals the substructure within hot-core sources.

10. SUMMARY AND CONCLUSIONS

The past decade has seen great advances in the simulation of hot-core chemistry. Significant efforts have been made to understand the formation of complex organic molecules in star-forming regions, in light of the apparent deficiency of gas-phase processes. As a result, a greater emphasis has been placed on the detailed treatment of grain-surface and bulk-ice processes and their interactions with the gas phase. Chemical kinetics models based on rate equations can be used to examine the complex chemistry of hot-core regions, and great advances have been made in the implementation of Monte Carlo simulations, although, in both cases, the treatment of detailed physical structure within the dust-grain ice mantles remains a challenge. Sophisticated models are now routinely used to combine gas-phase, grain-surface, and bulk-ice chemical treatments, while their integration with more realistic physical models of specific sources has become important for the simulation of molecular emission spectra.

Additionally, chemical networks used for hot-core models now incorporate chemistry of direct biological significance, including formation mechanisms for amino acids and sugars. The results of these modeling studies can be directly compared to the complexity observed with the newest generation of observational instruments, which provide quantitative information that can be benchmarked against the models.

Despite these successes, there remains a large gap between current modeling capabilities and the objective of a full, comprehensive model of star-formation environments. Chemical reaction networks are far from complete, and many of the parameters therein are educated guesses at best, while detailed treatments of ice structure are yet in their infancy. Likewise, physical models that properly account for the hydrodynamical processes occurring in hot cores have not yet been coupled with the more comprehensive chemical networks necessary to examine the chemistry of star-forming regions; indeed, the dynamics of high-mass star formation are currently a matter of

considerable debate. Nonetheless, the results from the current chemical models of hot cores are valuable tools for comparison with observations; the simulations agree well with observations for the most abundant molecular species, and advances in the translation of chemical model results into directly observable quantities will allow more specific predictions to be made for individual sources.

In the coming years, models of hot-core chemistry will need to advance and expand in several different directions, both to address current challenges and to incorporate new information from high-quality astronomical observations and chemical experiments. However, one might also expect that these advances will place yet greater technical demands on the computational models, some of which already operate close to the limits of feasible run times. The breadth of chemical and physical processes considered, and the resultant constraints placed upon the models, will require that astrochemists not be too dogmatic in the demand that every part of a model be state-of-the-art; even with the best computers in the world, such models of astrophysical sources will never be entirely comprehensive. The choice of whether detailed chemistry, detailed ice structure, detailed dynamics, and/or detailed radiative transfer are used must depend on the choice of problem and the abilities of individual scientists to best exploit their own capabilities. However, in spite of the inevitable incompleteness of astrochemical models, the past few years have demonstrated that the models can reliably reproduce many facets of the observational data, that they can explain the microscopic processes occurring on astronomical scales, and that they can be used to guide future observational strategies for hot-core sources.

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