On Cosmic-Ray-driven Grain Chemistry in Cold Core Models

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Abstract

In this paper, we present preliminary results illustrating the effect of cosmic rays on solid-phase chemistry in models of both TMC-1 and several sources with physical conditions identical to TMC-1 except for hypothetically enhanced ionization rates. Using a recent theory for the addition of cosmic-ray-induced reactions to astrochemical models, we calculated the radiochemical yields, called $G$ values, for the primary dust grain ice-mantle constituents. We show that the inclusion of this nonthermal chemistry can lead to the formation of complex organic molecules from simpler ice-mantle constituents, even under cold core conditions. In addition to enriching ice mantles, we find that these new radiation-chemical processes can lead to increased gas-phase abundances as well, particularly for HOCO, NO$_2$, HC$_3$O$_3$, methyl formate (HCOOCH$_3$), and ethanol (CH$_3$CH$_2$OH). These model results imply that HOCO—and perhaps NO$_2$—might be observable in TMC-1. Future detections of either of these two species in cold interstellar environments could provide strong support for the importance of cosmic-ray-driven radiation chemistry. The increased gas-phase abundance of methyl formate can be compared with abundances achieved through other formation mechanisms such as pure gas-phase chemistry and surface reactions.

Key words: astrochemistry – cosmic rays – ISM: abundances – ISM: clouds – ISM: molecules

1. Introduction

Cosmic rays are a form of high-energy (MeV–TeV) ionizing radiation composed mostly of protons thought to form both in supernovae and galactic nuclei (Lemaître & Vallarta 1933; Baade & Zwicky 1934; Blasi 2013). It has long been speculated that these energetic particles can have significant physicochemical effects on the interstellar medium (ISM) as a result of collisional energy transfer to the matter in a region. For example, in Herbst & Klemperer (1973), cosmic rays were shown to be the drivers of cold core chemistry via

$$H_2 \rightarrow H^+_2 + e^-$$ (1)

followed by

$$H^+_2 + H_2 \rightarrow H^+_3 + H,$$ (2)

where the curly arrow implies bombardment by an energetic particle. The ion–molecule reactions initiated by H$_3^+$ are of central importance in the subsequent formation of polyatomic species. In addition, cosmic rays are thought to play an important role both in source heating (Goldsmith & Langer 1978; Ao et al. 2013) and in generating internal UV photons in cold cores through the Lyman and Werner band excitation of H$_2$ (Prasad & Tarafdar 1983).

The Galactic value of the cosmic-ray ionization rate, $\zeta$, cannot be directly measured from Earth due to the effects of the solar wind (Parker 1958). It is thought that the most common ionization rate in the ISM is $\zeta \approx 10^{-15}$ s$^{-1}$ everywhere but in dense regions (Grenier et al. 2015), where interactions between the dense cloud and the charged particles that comprise cosmic rays result in a reduced ionization rate of $\approx 10^{-17}$ s$^{-1}$ (Rimmer et al. 2012). However, even in dense regions, local effects can result in substantially higher fluxes of ionizing radiation leading to ionization rates in the range $\zeta \approx 10^{-15} - 10^{-14}$ s$^{-1}$. Such rates arise in Sgr A* (Ao et al. 2013; Yusef-Zadeh et al. 2013a, 2013b), and in sources like W51C, which are near supernova remnants (Ceccarelli et al. 2011; Shingledecker et al. 2016).

Collisions between cosmic rays and dust grains are also important in the ISM. For instance, Ivlev et al. (2015) note that cosmic rays affect the net charge on dust particles, which has an influence on grain growth. Cosmic-ray collisions have also been implicated in impulsive grain heating (Hasegawa & Herbst 1993; Ivlev et al. 2015b), which can stimulate both diffusive chemistry and desorption. Despite this, the direct chemical effects resulting from cosmic-ray bombardment of dust grain ice mantles are not currently considered in astrochemical models. Previous experimental work has shown that the bombardment of low-temperature ices by ionizing radiation can trigger a rich chemistry (Hudson & Moore 2001; Abplanalp et al. 2016; Rothard et al. 2017)—including the formation of complex organic molecules such as amino acids (Holtom et al. 2005; Lafrasse et al. 2006; Hudson et al. 2008).

Following Bohr (1913), the energy lost by an energetic particle per distance traveled—called the stopping power—can be approximated by the sum of two types of energy loss, as seen in the following equation:

$$\frac{dE}{dx} = n(S_n + S_e),$$ (3)

where $n$ is the density of the target material, while $S_n$ and $S_e$ are so-called stopping cross sections (Ziegler & Biersack 1985; Johnson 1990)—also known as energy loss functions, in units of area × energy (Peterson & Green 1968). Here, $S_n$ characterizes the elastic energy collisionally transferred to nuclei in a material, while $S_e$ characterizes the energy transferred to electrons in inelastic collisions (Bohr 1913; Johnson 1990; Spinks & Woods 1990). Inelastic events, in turn, are typically approximated as consisting of collisions that cause either the ionization or electronic excitation of target species. The ionization of species in a material results in the...
formation of so-called “secondary electrons” (Spinks & Woods 1990). Around $10^5$ secondary electrons can be produced per MeV transferred to a material, and they play a critical role in propagating physicochemical changes initiated by primary ions (Spinks & Woods 1990; Gerakines et al. 2001; Mason et al. 2014).

In Abplanalp et al. (2016), we made the first attempt—to the best of our knowledge—to incorporate experimentally determined chemical reactions resulting from radiation processes into an astrochemical model. Based on insights gained both from that work and from radiation chemistry based on a subsequent detailed microscopic Monte Carlo model (Shingledecker et al. 2017), we developed a general method described in detail in Shingledecker & Herbst (2018) targeted at the great majority of astrochemically relevant radiolysis processes that have not been studied in detail in the laboratory. The basis of this method is that a microscopic collision between a target species, $A$, and either a primary ion or secondary electron is assumed to have one of the following outcomes:

$$A \rightarrow A^+ + e^{-}, \quad (R1)$$

$$A \rightarrow A^+ + e^{-} \rightarrow A^* \rightarrow bB^* + cC^*, \quad (R2)$$

$$A \rightarrow A^* \rightarrow bB + cC, \quad (R3)$$

$$A \rightarrow A^+. \quad (R4)$$

Here, the asterisk indicates an electronically excited species, which can be referred to as “suprathermal” (Abplanalp et al. 2016); $B$ and $C$ are the dissociation products; and the lowercase letters are the stoichiometric coefficients (Spinks & Woods 1990). In this work, we will refer to molecular dissociation due to bombardment by ionizing radiation as radiolysis (Spinks & Woods 1990; Johnson 2011).

In processes (R1) and (R2), $A$ is ionized upon collision with an energetic particle, resulting in the ion pair $A^+ + e^{-}$, which can quickly undergo dissociative recombination, as shown in (R2). The relative importance of (R1) and (R2) is characterized by the electron escape probability, $P_e$, which we will here assume to be zero for solid-phase processes, so that (R1) is negligible. In processes (R3) and (R4), $A$ is electronically excited after collision with an energetic particle. As with the ionizing processes, (R1) and (R2), the relative importance of (R3) and (R4) is given by $P_{dis}$, the dissociation probability, which we will here assume to be 0.5 in the absence of relevant experimental or theoretical values. Based on results from previous, more detailed Monte Carlo modeling of radiation chemistry (Shingledecker et al. 2017), we have assumed that the intermediate species $A^*$ produced via (R2) dissociates immediately with unit probability, unlike in process (R3), due to the greater exothermicity of dissociative recombination.

The suprathermal species produced in processes (R2) and (R4) are critical when considering the effects of radiation exposure on a material, particularly in cold regions, because their energies are often sufficient to overcome reaction barriers that are inaccessible to the reactants in their ground electronic states (Spinks & Woods 1990). Previous experimental work suggests that these electronically excited species can drive the formation of complex organic molecules, even in solids at 5 K (Abplanalp et al. 2016), where they likely either rapidly react with a neighbor or are quenched by the material (Spinks & Woods 1990).

The overall efficiency of processes (R1)–(R4), called the radiochemical yield, is characterized by the $G$ value (Dewhurst et al. 1952), defined as the number of molecules created or destroyed per 100 eV deposited by an incident energetic particle into some system. As described in detail in Shingledecker & Herbst (2018), the $G$ values for processes (R1)–(R4) can be calculated using the following expressions:

$$G_{R1} = P_e \left( \frac{100 \text{ eV}}{W} \right), \quad (4)$$

$$G_{R2} = (1 - P_e) \left( \frac{100 \text{ eV}}{W} \right), \quad (5)$$

$$G_{R3} = P_{dis} \left( \frac{100 \text{ eV}}{W} \right) \left( \frac{W - (E_{ion} + W_e)}{W_{exc}} \right), \quad (6)$$

$$G_{R4} = (1 - P_{dis}) \left( \frac{100 \text{ eV}}{W} \right) \left( \frac{W - (E_{ion} + W_e)}{W_{exc}} \right), \quad (7)$$

where $W$ is the mean energy per ion pair (usually ~30 eV; Dalgarno & Grifﬁng 1958; Edgar et al. 1973), $E_{ion}$ is the ionization energy of $A$, $W_{exc}$ is the average excitation energy of $A$, and $W_s$ is the average subexcitation energy of the secondary electrons formed via the ionization of $A$ (typically ~3 eV; Elkomoss & Magee 1962; Fueki & Magee 1963).

By deﬁnition, there is one ionization per ion pair; however, the number of excitations per ionization, $\xi$, is given by

$$\xi = \frac{W - (E_{ion} + W_e)}{W_{exc}} \quad (8)$$

and is the extra factor included in Equations (6) and (7). Physically, for every W eV lost per ion pair, an amount equal to $E_{ion}$ of that energy is used to generate the ion pair, and some small amount $W_s$ accounts for the fact that secondary electrons (a) lose energy through inelastic collisions or (b) have insufficient energy upon formation to either ionize or excite species in the material. Thus, the remaining energy per ion pair available to cause electronic excitations is $W - (E_{ion} + W_e)$, and $\xi$, the average number of excitations that can result from this amount of energy, is a function of the average excitation energy, $W_{exc}$.

These $G$ values can, in turn, be used to estimate the first-order rate coefficients ($s^{-1}$) of processes (R1)–(R4) via

$$k_{R1} = G_{R1} \left( \frac{S_e}{100 \text{ eV}} \right) \left( \frac{\xi}{10^{-17}} \right), \quad (9)$$

$$k_{R2} = G_{R2} \left( \frac{S_e}{100 \text{ eV}} \right) \left( \frac{\xi}{10^{-17}} \right), \quad (10)$$

$$k_{R3} = G_{R3} \left( \frac{S_e}{100 \text{ eV}} \right) \left( \frac{\xi}{10^{-17}} \right), \quad (11)$$

$$k_{R4} = G_{R4} \left( \frac{S_e}{100 \text{ eV}} \right) \left( \frac{\xi}{10^{-17}} \right). \quad (12)$$

Here, $\phi_{ST}$ is the integrated Spitzer–Tomasko cosmic-ray flux (8.6 particles cm$^{-2}$ s$^{-1}$) (Spitzer & Tomasko 1968), $\xi$ is the H$_2$ ionization rate, and $S_e$ is the electronic stopping cross section (Bethe 1932; Ziegler & Biersack 1985; Johnson 1990).
Amorphous H2O is typically the dominant ice-mantle constituent; thus, we approximate the stopping cross section for protons in amorphous water ice with the more readily available values for liquid water, which were calculated using the PSTAR program.\(^4\) An average value of \(S_e = 1.287 \times 10^{-15} \text{ cm}^2 \text{ eV}^{-1}\) was obtained using the Spitzer–Tomasko cosmic-ray flux (Spitzer & Tomasko 1968). One can estimate the effect of going from a water ice to, for example, one comprised mainly of CO using the ratio of stopping cross sections for the two species. Using the Bethe equation for the electronic stopping cross section (Bethe 1932)—and all else being equal—\(S_e \text{ CO} \approx 1.4 \times S_e \text{ H}_2 \text{ O}\)—which may not have a significant effect in most astrochemical models. As discussed further in Section 3, when multiplied by the density of the reactant species, Equations (9)–(12) refer to the time dependence of the concentration of products produced by radiolysis—driven mainly by inelastic collisions involving secondary electrons.

We here examine how radiolysis of the primary dust grain ice-mantle constituents influences the chemistry of cold cores like TMC-1. The organization of the rest of this paper is as follows: In Section 2, we give details concerning the code and physical conditions used here, while Section 3 contains a description of the reactions and processes added to the network for this work. Section 4 contains a description and discussion of our major findings, while in Section 5, we summarize our results and point to areas of future development.

### 2. Model

In this work, we focus on the chemistry of cold cores, such as TMC-1. Despite the low temperatures of these regions, their chemical complexity has been highlighted by recent detections of species such as HC3N (McGuire et al. 2017), HC3O (Cordiner et al. 2017; McGuire et al. 2017), and the aromatic molecule C6H5CN (McGuire et al. 2018). The effects of radiation chemistry should be more pronounced in these cold interstellar environments since thermal diffusion is inhibited, thus increasing the relative importance of fast solid-phase reactions involving suprathermal species.

We utilized the NAUTILUS-1.1 astrochemical model (Ruaud et al. 2016), in which three phases are simulated, specifically, (a) the gas-phase, (b) the ice/grain-surface, and (c) the ice-mantle bulk. This distinction between the surface and bulk of the ice is helpful here because it highlights an important aspect of solid-phase radiation chemistry, namely, that bombardment by ionizing radiation can greatly increase the chemical importance of the bulk ice, since this is the phase in which the majority of the physiochemical changes likely occur (Johnson 1990; Spinks & Woods 1990; Shingledecker et al. 2017). The degree of penetration into the ice constitutes a major difference between photochemistry and radiation chemistry (Gerakines et al. 2001, 2004). In the absence of bombardment by energetic particles, the surface is significantly more important in astrochemical models, due both to the lower diffusion barriers and direct contact with the surrounding gas. The nonthermal desorption mechanisms for surface species are (1) chemical desorption with a standard 1% efficiency (Garrod et al. 2007), (2) cosmic-ray-induced desorption (Hasegawa & Herbst 1993), and (3) photodesorption (Bertin et al. 2013).

We ran simulations of two different types of sources, the cold core TMC-1 and a group of hypothetical sources that are physically identical to TMC-1 aside from having higher ionization rates. The latter set of simulations was run in order to identify any trends in our models arising from the included radiation chemistry. The physical conditions used here for both sets of simulations are given in Table 1, and all models utilized the same initial elemental abundances, which are listed in Table 2.

### 3. Network

Our three-phase chemical network is based on the one described in Ruaud et al. (2016) to which we have added the gas-phase reactions of Balucani et al. (2015). To this network, we have included both (a) dissociation pathways for the major ice-mantle constituents due to collisions with cosmic rays or secondary electrons and (b) reactions involving the suprathermal products. Radiochemical yields (\(G\) values) and rate coefficients were calculated using the Shingledecker–Herbst method, and are a function of \(E_{\text{ion}}, W_{\text{exc}},\) and \(W_c\). Values for the ionization energy, \(E_{\text{ion}}\), were taken from the NIST Chemistry Webbook (Lias 2018). The average electronic excitation energies, \(W_{\text{exc}}\), were estimated from the strongest UV–Vis absorption for each species (Fueki & Magee 1963; Shingledecker & Herbst 2018) based on spectra in the MPI-Mainz UV–Vis Spectral Atlas (Keller-Rudek et al. 2013). Finally, the average subexcitation electron energies were calculated using the method

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\(\text{\footnotesize Notes.}\)

1. Wakeham & Herbst (2008).
2. McGuire et al. (2018).
3. Jenkins (2009).
4. Graedel et al. (1982).
5. Neufeld et al. (2005).

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### Table 1

| Parameter | TMC-1 | Hypothetical Sources |
|-----------|-------|----------------------|
| \(n_1 (\text{cm}^{-3})\) | \(10^4\) | \(10^4\) |
| \(n_{\text{H}_{2}O} (\text{cm}^{-3})\) | \(1.8 \times 10^{-8}\) | \(1.8 \times 10^{-8}\) |
| \(T_{\text{gas}} (\text{K})\) | 10 | 10 |
| \(T_{\text{grain}} (\text{K})\) | 10 | 10 |
| \(A_e (\text{mag})\) | 10 | 10 |
| \(N_{\text{H}_{2}O} (\text{cm}^{-2})\) | \(1.5 \times 10^{15}\) | \(1.5 \times 10^{15}\) |
| \(\zeta (\text{s}^{-1})\) | \(10^{-17}\) | \(10^{-17} - 10^{-14}\) |

### Table 2

| Element | Value |
|---------|-------|
| \(X(\text{H}_2)\) | \(5.00 \times 10^{-1}\) |
| \(X(\text{He})\) | \(9.00 \times 10^{-2}\) |
| \(X(\text{N})\) | \(2.14 \times 10^{-3}\) |
| \(X(\text{O})\) | \(1.70 \times 10^{-4}\) |
| \(X(\text{Cl})\) | \(1.70 \times 10^{-4}\) |
| \(X(\text{S})\) | \(8.00 \times 10^{-5}\) |
| \(X(\text{Si})\) | \(8.00 \times 10^{-9}\) |
| \(X(\text{Fe})\) | \(3.00 \times 10^{-9}\) |
| \(X(\text{Na})\) | \(2.00 \times 10^{-9}\) |
| \(X(\text{Mg})\) | \(7.00 \times 10^{-9}\) |
| \(X(\text{P})\) | \(2.00 \times 10^{-10}\) |
| \(X(\text{Cl})\) | \(1.00 \times 10^{-9}\) |
| \(X(\text{F})\) | \(6.68 \times 10^{-9}\) |

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\(\text{\footnotesize Notes.}\)

1. Wakeham & Herbst (2008).
2. McGuire et al. (2018).
3. Jenkins (2009).
4. Graedel et al. (1982).
5. Neufeld et al. (2005).
of ElKomoss & Magee (1962). A list of both the species that undergo radiolysis as well as the associated parameters used in calculating rate coefficients are given in Table 3, while Table 4 lists the solid-phase radiolysis pathways for each species.

In our models, we assume that the processes in Table 4 occur both on the surface and in the ice mantle and have labeled them Types I, II, and III. Type I radiolysis corresponds to the process given in Equation (R2), where species A is ionized and recombines with the newly formed electron to produce suprathermal dissociation products. Type II processes correspond to the sequence of events given in Equation (R3), where A dissociates into thermal products after being collisionally excited by an energetic particle. Finally, Type III processes are characterized by Equation (R4), where A is collisionally excited, but does not immediately dissociate.

As supported by previous experimental work (Bennett & Kaiser 2005; Abplanalp et al. 2016; Bergantini et al. 2018), we assume that for a suprathermal species $B^*$, the lifetime in solids is much shorter ($\ll 1$ s) than the average surface or bulk thermal hopping time, $t_{\text{hopping}}$ ($\approx 1$ s at 10 K; Hasegawa et al. 1992). As noted by Bennett & Kaiser (2005), the short lifetimes of these suprathermal species, relative to their hopping times at low temperatures, means that their solid-phase chemistry is likely dominated by reactions with neighbors. Therefore, we assume that once formed, suprathermal species only either react or relax back to the ground state. For reactions of the form

$$A + B^* \rightarrow \text{products},$$  

we use the following formula for calculating the rate coefficients, $k_{\text{ST}}$(cm$^3$ s$^{-1}$):

$$k_{\text{ST}} = f_{\text{br}} \left[ \frac{v_0^A + v_0^B}{N_{\text{site}}n_{\text{dust}}} \right],$$  

where $f_{\text{br}}$ is the product branching fraction, $n_{\text{dust}}$ is the dust density—here equal to $1.8 \times 10^{-8}$ cm$^{-3}$, $N_{\text{site}}$ is the number of physisorption sites on the grain—here equal to $1.5 \times 10^{15}$ cm$^{-2}$, and $v_0^X$ is the characteristic vibrational frequency for some physisorbed species, $X$, which is typically in the range of $(1-3) \times 10^{-12}$ s$^{-1}$ (Herbst & Millar 2008). This frequency can

### Table 3

| Species | $E_{\text{cm}}$ (eV) | $W^*_{\text{cm}}$ (eV) | $W_e$ (eV) |
|---------|----------------------|----------------------|------------|
| H$_2$O  | 12.621               | 11.190               | 3.824      |
| O$_2$   | 12.070               | 8.500                | 3.886      |
| O$_3$   | 12.530               | 4.860                | 3.815      |
| CO      | 14.014               | 13.190               | 3.947      |
| CO$_2$  | 13.777               | 13.776               | 3.927      |
| NO      | 9.264                | 13.776               | 3.422      |
| NO$_2$  | 9.586                | 21.377               | 3.478      |
| O$_2$H  | 11.350               | 5.961                | 3.694      |
| H$_2$O$_2$ | 10.580             | 10.332               | 3.606      |
| CH$_3$OH| 10.840               | 14.760               | 3.636      |
| NH$_3$  | 10.070               | 9.110                | 3.542      |
| H$_2$CO | 10.880               | 7.940                | 3.641      |
| CH$_4$  | 12.610               | 13.000               | 3.823      |
| CH$_3$COCH$_3$ | 9.703   | 6.358               | 3.494      |

### Table 4

| Number | Process | $f_{\text{br}}$ | $G$-value | Type |
|--------|---------|-----------------|-----------|------|
| 1      | H$_2$O  | 0.500           | 3.704     | I    |
| 2      | H$_2$O + OH$^*$ + H$^*$ | 0.500 | 3.704 | I |
| 3      | H$_2$O + OH + H | 1.000 | 1.747 | II |
| 4      | H$_2$O + H$_2$O | 1.000 | 1.747 | III |
| 5      | O$_2$ + O$^*$ | 1.000 | 3.704 | I |
| 6      | O$_2$ + O + O$^*$ | 1.000 | 2.138 | II |
| 7      | O$_2$ + O$_2^*$ | 1.000 | 2.138 | III |
| 8      | O$_2$ + O$_2^*$ + O$^*$ | 1.000 | 3.704 | I |
| 9      | O$_2$ + O + O$^*$ | 1.000 | 4.059 | II |
| 10     | O$_2$ + O$_2^*$ + O$^*$ | 1.000 | 4.059 | III |
| 11     | CO + C$^*$ + O$^*$ | 1.000 | 3.704 | I |
| 12     | CO + C + O | 1.000 | 1.269 | II |
| 13     | CO + CO$^*$ | 1.000 | 1.269 | III |
| 14     | CO$_2$ + CO$^*$ + O$^*$ | 1.000 | 3.704 | I |
| 15     | CO$_2$ + CO + O | 1.000 | 1.249 | II |
| 16     | CO$_2$ + CO$_2^*$ | 1.000 | 1.249 | III |
| 17     | NO + N$^*$ + O$^*$ | 1.000 | 3.704 | I |
| 18     | NO + N + O | 1.000 | 1.922 | II |
| 19     | NO + NO$^*$ | 1.000 | 1.922 | III |
| 20     | NO + NO$^*$ + O$^*$ | 1.000 | 3.704 | I |
| 21     | NO + NO + O | 1.000 | 1.207 | II |
| 22     | NO + NO$_2^*$ | 1.000 | 1.207 | III |
| 23     | O$_2$ + OH$^*$ + O$^*$ | 1.000 | 3.704 | I |
| 24     | O$_2$ + OH + O | 1.000 | 3.714 | II |
| 25     | O$_2$ + O$_2$H$^*$ | 1.000 | 3.714 | III |
| 26     | H$_2$O$_2$ + OH + OH$^*$ | 0.500 | 3.704 | I |
| 27     | H$_2$O$_2$ + O$^*$ + H$_2$O$^*$ | 0.500 | 3.704 | I |
| 28     | H$_2$O$_2$ + OH + OH$^*$ | 1.000 | 2.296 | II |
| 29     | NH$_3$ | 0.500 | 3.704 | I |
| 30     | NH$_3$ + H$^*$ + NH$_2^*$ | 0.500 | 3.704 | I |
| 31     | NH$_3$ + H + NH$_2$ | 1.000 | 2.721 | II |
| 32     | NH$_3$ + NH$_2^*$ | 1.000 | 2.721 | III |
| 33     | CH$_4$ + H$^*$ + CH$_4^*$ | 0.500 | 3.704 | I |
| 34     | CH$_4$ + H + CH$_4^*$ | 0.500 | 3.704 | I |
| 35     | CH$_4$ + H + CH$_4$ | 1.000 | 1.505 | II |
| 36     | CH$_4$ + CH$_4^*$ | 1.000 | 1.505 | III |
| 37     | H$_2$CO + H$^*$ + HCO$^*$ | 1.000 | 3.704 | I |
| 38     | H$_2$CO + H + HCO | 1.000 | 2.910 | II |
| 39     | H$_2$CO + H$_2$CO$^*$ | 1.000 | 2.910 | I |
| 40     | CH$_3$OH + H$^*$ + CH$_3$OH$^*$ | 0.333 | 3.704 | I |
| 41     | CH$_3$OH + H + CH$_3$OH$^*$ | 0.333 | 3.704 | I |
| 42     | CH$_3$OH + OH$^*$ + CH$_3$OH$^*$ | 0.333 | 3.704 | I |

Notes.

a Liis (2018).
b Keller-Rudek et al. (2013).
The suprathermal reactions we have added to our network can be grouped into two classes. Class 1 refers to those that are similar to reactions involving ground-state species already included in the network, while Class 2 refers to novel reactions unlike those currently included for thermal species. To illustrate Class 1 reactions, consider the following example:

\[
H(s) + CO(s) \rightarrow HCO(s),
\]

which has an activation energy of 2300 K in the Ruaud et al. (2016) network, in addition to a diffusion barrier. Here, \(s\) indicates either a surface or bulk species. We will later use \(g\) to denote gaseous species, and in cases where reactants labeled with \(s\) lead to products in the gas phase, the reactants are assumed to be surface species only. Here we include the following Class 1 suprathermal reactions based on (18):

\[
H^*(s) + CO(s) \rightarrow HCO(s) \quad (19)
\]

\[
H(s) + CO^*(s) \rightarrow HCO(s). \quad (20)
\]

We assume no barrier for both reactions (19) and (20), as implied by results from ice irradiation experiments (Abplanalp et al. 2016). Rate coefficients for reactions (19) and (20), as well as for all similar Class 1 suprathermal reactions, are calculated in our model using Equation (14). Another group of Class 1 reactions included in our network are based on work by Hudson (2017), who found ketene \((H_2CCO)\) among the products of acetone irradiation, which could form via

\[
CH_3 + CH_2CO \rightarrow H_2CCO + CH_4, \quad (21)
\]

where the \(CH_3\) and \(CH_2CO\) radicals result from either Type I or II radiolysis of acetone. We have included both the reaction between ground-state radicals as well as reactions involving a single suprathermal reactant, similar to reactions (19) and (20). A full list of these new reactions is available from the authors.

Class 2 is used to categorize novel reactions that are unlike the kinds of thermal reactions typically considered in gas/grain

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**Table 4**

| Number | Process | \(j_b\) | G-value | Type |
|--------|---------|---------|---------|------|
| 43     | CH\(_3\)OH \(\rightarrow\) H + CH\(_3\)O | 0.33 | 1.571 | II |
| 44     | CH\(_3\)OH \(\rightarrow\) H + CH\(_2\)OH | 0.33 | 1.571 | II |
| 45     | CH\(_3\)OH \(\rightarrow\) OH + CH\(_3\) | 0.33 | 1.571 | II |
| 46     | CH\(_2\)OH \(\rightarrow\) CH\(_3\)OH\(^*\) | 1.00 | 1.571 | III |
| 47     | CH\(_3\)COCH\(_3\) \(\rightarrow\) CH\(_3\) + CH\(_2\)O\(^*\) | 1.00 | 3.704 | I\(^b\) |
| 48     | CH\(_3\)COCH\(_3\) \(\rightarrow\) CH\(_3\) + CH\(_2\)CO | 1.00 | 4.020 | II |
| 49     | CH\(_3\)COCH\(_3\) \(\rightarrow\) CH\(_3\)COCH\(_3\)\(^*\) | 1.00 | 4.020 | III |

**Notes.**

\(^a\) Bergantini et al. (2018).

\(^b\) Hudson (2017).

The characteristic frequency, \(\nu_0\), is given by

\[
\nu_0 = \sqrt{\frac{2N_{\text{site}}E_b^X}{\pi^2m_X}}, \tag{15}
\]

where \(m_X\) is the mass of \(X\) and \(E_b^X\) is the diffusion barrier, which here we set equal to 40\% and 80\%—for surface and bulk species, respectively—of the desorption energies used in Ruaud et al. (2016). Since the dominant mechanism for reactions involving suprathermal species in solids is likely not diffusive (Bennett & Kaiser 2005), Equation (14) is similar to the typical solid-phase bimolecular rate coefficients, but differs from them in that it does not contain either \((a)\) a Boltzmann term characterizing thermal hopping or \((b)\) a factor accounting for tunneling through reaction barriers, since we assume that suprathermal species are sufficiently energetic to react without a barrier (Hasegawa et al. 1992).

In addition to destruction through chemical reactions, we also assume that suprathermal species can be quenched by the ice mantle (Spinks & Woods 1990; Bennett & Kaiser 2005), i.e.,

\[
B^* + M \rightarrow B + \text{M}. \tag{16}
\]

We use the characteristic frequency, \(\nu_0\), as a pseudo first-order approximation for the rate coefficient of the above process. Here, we have assumed that quenching by the solid is very fast \((\sim 10^{-14} \text{ s})\) compared to spontaneous emission \((\sim 10^{-9} \text{ s})\) and thus have neglected it as a de-excitation channel in this work.

To illustrate how this radiation chemistry is incorporated into our chemical network, consider the formation and destruction of the suprathermal species, \(B^*\), which is produced solely via process (R2) and only reacts with \(A\), as in Equation (13). In this example, the rate of change of \(n(B^*)\) is given by the equation

\[
\frac{d}{dt}n(B^*) = k_{R2n}(A) - \nu_0^B n(B^*) - k_{\text{ST}} n(A)n(B^*), \tag{17}
\]

where the first term on the right gives the production of \(B^*\) via the radiolysis of \(A\), the second term gives the quenching rate for \(B^*\), and the third term gives the rate of destruction via reaction with \(A\)—with \(k_{\text{ST}}\) being the rate coefficient for suprathermal reactions given in Equation (14). We emphasize that in our actual network, most suprathermal species are produced from the radiolysis of more than one species, and all have more than one destructive reaction.

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**Table 5**

| Number | Reaction | \(j_b\) | Source |
|--------|----------|---------|--------|
| 50     | C\(^*\) + H\(_2\)O \(\rightarrow\) CH + OH | 1.0 | Mayer et al. (1967) |
| 51     | C\(^*\) + CO \(\rightarrow\) CCO | 1.0 | Hussain & Kirsch (1971) |
| 52     | C\(^*\) + CH\(_3\)OH \(\rightarrow\) CH\(_3\)CHO | 0.5 | Shannon et al. (2014) |
| 53     | C\(^*\) + CH\(_3\)OH \(\rightarrow\) CH\(_3\) + HCO | 0.5 | Shannon et al. (2014) |
| 54     | O\(^*\) + CH\(_4\) \(\rightarrow\) CH\(_3\)OH | 0.65 | Bergner et al. (2017) |
| 55     | O\(^*\) + CH\(_4\) \(\rightarrow\) H\(_2\)CO + H\(_2\) | 0.35 | Bergner et al. (2017) |
| 56     | O\(^*\) + CH\(_3\)OH \(\rightarrow\) CH\(_3\) + HCO | 1.0 | Matsumi et al. (1994) |
| 57     | O\(^*\) + NO \(\rightarrow\) NO\(_2\) | 1.0 | Atkinson et al. (2004) |

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| Number | Process | \(j_b\) | Source |
|--------|---------|---------|--------|
| 58     | CH\(_3\)\(^*\) + CH\(_2\)O \(\rightarrow\) CH\(_2\)CH\(_2\)OH | 0.5 | Bergantini et al. (2018) |
| 59     | CH\(_2\)\(^*\) + CH\(_3\)OH \(\rightarrow\) CH\(_2\)CH\(_3\)O | 0.5 | Bergantini et al. (2018) |
To illustrate why this type of chemistry is astrochemically interesting, consider the following Class 2 reaction:

\[
\text{O}(s) + \text{CH}_4(s) \rightarrow \text{CH}_3\text{OH}(s). \tag{22}
\]

This type of reaction is known as an “insertion” since the oxygen atom is inserted into one of the C-H bonds to form methanol. Reaction (22) is highly endothermic, having an activation energy of \(\sim 4300 \text{ K} \) (Baulch et al. 1992); however, Bergner et al. (2017) recently found that \(\text{O}(1D)\) and methane could efficiently react to form methanol in low-temperature ices via this mechanism. Further evidence for the importance of solid-phase irradiation-driven insertion reactions comes from recent work by Bergantini et al. (2018), who found that such processes could lead to ethanol and dimethyl ether formation at low temperatures. Thus, Class 2 reactions may contribute to the formation of COMs, even in cold interstellar environments.

In this study, we added Class 2 reactions for both \(\text{C}^+\) and \(\text{O}^+\), as listed in Table 6. Most of these new reactions were drawn from combustion chemistry. Since cosmic rays, such as other forms of ionizing radiation, produce highly nonthermal species, some of the endothermic reactions previously considered in the context of high-temperature systems become relevant when considering irradiated low-temperature ices.

We have also included gas-phase destruction reactions for HOCO. In addition to photodissociation by internal and external UV photons, the reactions listed in Table 6 were added to the Ruaud et al. (2016) network, with neutral–neutral rate coefficient parameters given in terms of \(\alpha\), \(\beta\), and \(\gamma\) using the Arrhenius–Kooki formula

\[
k_{\text{AK}} = \alpha \left( \frac{T_{\text{gas}}}{300 \text{ K}} \right)^3 \exp \left( -\frac{\gamma}{T_{\text{gas}}} \right), \tag{23}
\]

where \(T_{\text{gas}}\) is the kinetic temperature of the gas.

For reactions between the polar neutral HOCO and ions, we use the Su-Chesnavich capture theory (see Woon & Herbst 2009 and references therein). For HOCO, values of \(\mu_1 = 3.179 \text{ D}\) and \(\alpha_2 = 2.739 \text{ Å}^2\) were utilized for the dipole and dipole polarizability, respectively (Johnson 2016).

### 4. Results and Discussion

Given the relative novelty of the radiation chemistry we have added to our chemical network, it is natural to question what effect these new reactions will have on the abundances of important cold core species. To that end, in Figure 1, we show the calculated abundances of the cyanopolyynes in our TMC-1 models, both with and without the new reactions listed in Tables 4 and 5. Reassuringly, one can see that there are no significant differences between cyanopolyne abundances in the two sets of results—a key test since modern astrochemical models are typically able to reproduce the observed abundances of these species quite well (McGuire et al. 2017).

Since cyanopolyynes are formed in the gas phase (Loomis et al. 2016), and all of the radiolysis processes considered in this work are assumed to take place in or on the surface of dust grain ice mantles, a better confirmation of the new chemistry may be to examine the abundance of the primary ice-mantle constituent, namely, water. Therefore, in Figure 2, we show the abundance of water in the gas phase, ice surface, and ice bulk in our TMC-1 models both with and without radiation chemistry. Again, we find that the differences between the two are negligible. Thus, the addition of the novel reactions does not lead to unphysical predictions for common species (e.g., water), nor does it obviously degrade our ability to reproduce the abundances of commonly observed molecules such as the cyanopolyynes.

However, we have found that the addition of cosmic-ray-driven reactions does indeed have a significant effect on the abundances of a number of astrochemically interesting species in our model. In the remainder of this section, we will describe how the inclusion of radiation chemistry affects HOCO, NO\(_2\), HC\(_5\)O\(_2\), and HCOOC\(_3\)H\(_2\), which showed the most pronounced enhancements in gas-phase abundance.

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**Table 6**

| Number | Reaction                                      | \(\alpha\) \(\times 10^{-11}\) | \(\beta\) | \(\gamma\) | Source                        |
|--------|----------------------------------------------|-------------------------------|------|--------|-------------------------------|
| 60     | \(\text{HOCO} + \text{Cl} \rightarrow \text{HCl} + \text{CO}_2\) | 4.800                         | 0.000 | 0.000 | Li et al. (2000)              |
| 61     | \(\text{HOCO} + \text{O}_2 \rightarrow \text{O}_2\text{H} + \text{CO}_2\) | 1.900                         | 0.000 | 0.000 | Poggi & Francisco (2004)      |
| 62     | \(\text{HOCO} + \text{NO} \rightarrow \text{HNO} + \text{CO}_2\) | 2.450                         | 0.000 | 0.000 | Poggi & Francisco (2004)      |
| 63     | \(\text{HOCO} + \text{O} \rightarrow \text{OH} + \text{CO}_2\) | 1.440                         | 0.000 | 0.000 | Yu et al. (2007)              |
| 64     | \(\text{HOCO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CO}_2\) | 1.030                         | 0.000 | 0.000 | Yu et al. (2005)              |
| 65     | \(\text{HOCO} + \text{CH}_3 \rightarrow \text{H}_2\text{O} + \text{H}_2\text{C}_2\text{O}\) | 5.800                         | 0.000 | 0.000 | Yu & Francisco (2009)         |

**Notes.**

a See Equation (23).

b See Woon & Herbst (2009).
4.1. HOCO

As shown in Figure 3, abundances of HOCO are increased in simulations including radiation chemistry in the three phases of the model: gas, ice surface, and ice bulk. This increase is due primarily to the following surface reaction

\[ \text{OH}^\text{h}\,(s) + \text{CO}(s) \rightarrow \text{HOCO}(g), \]

where the HOCO product undergoes chemical desorption (Garrod et al. 2007). Here, surface abundances of CO are primarily the result of the adsorption from the gas phase, and OH\(^*\) is primarily formed via the Type I radiolysis of water

\[ \text{H}_2\text{O}(s) \rightarrow \text{OH}^\text{h}\,(s) + \text{H}^\text{h}\,(s). \]

The fact that HOCO is significantly enhanced in our TMC-1 simulations is notable because this species is more commonly encountered in high-temperature combustion chemistry (Smith & Zellner 1973; McCarthy et al. 2016); however, in Milligan & Jacox (1971)—perhaps the first work to identify HOCO—this species was detected in a mixed H\(_2\)O:CO ice after irradiation by VUV photons, underscoring the similarity between the products of both combustion and radiation (or high-energy photo-) chemistry. Thus, the detection of species like HOCO in a cold interstellar region would be a strong indication of cosmic-ray-induced radiation chemistry at work.

As shown in Figure 3(a), the peak gas-phase fractional abundance of HOCO is \(\sim 10^{-11}\). Assuming a hydrogen column density for TMC-1 of \(N(\text{H}_2) \approx 10^{22} \text{ cm}^{-2}\) (Gratier et al. 2016) results in a predicted HOCO column of \(N(\text{HOCO}) \approx 10^{11} \text{ cm}^{-2}\). Since HOCO has a dipole of \(\sim 3\) Debye (Johnson 2016), these model results imply that this species is potentially observable in TMC-1.

4.2. NO\(_2\)

NO\(_2\) is another species the abundance of which is enhanced in simulations that include radiation chemistry. As shown in Figure 4, as for the case of HOCO, NO\(_2\) abundances are increased in all three model phases, although the connection between these enhancements and radiation chemistry is slightly more complex than in the case of HOCO.
At early times (<10^4 years), the dominant formation route for gas-phase NO_2 is the reaction

\[ \text{NO}(g) + \text{O}_2\text{H}(g) \rightarrow \text{NO}_2(g) + \text{OH}(g). \]  

Here, gas-phase O_2H abundances are enhanced via

\[ \text{O}(s) + \text{OH}^*(s) \rightarrow \text{O}_2\text{H}(g). \]  

At later times in the TMC-1 simulations, the dominant formation routes for NO_2 are

\[ \text{O}(s) + \text{NO}^*(s) \rightarrow \text{NO}_2(g) \]  
\[ \text{O}^*(s) + \text{NO}(s) \rightarrow \text{NO}_2(g). \]

At all simulation times, surface NO^* is formed mainly via the Type III excitation of NO:

\[ \text{NO}(s) \rightarrow \text{NO}^*(s). \]

while O^* is formed from the Type I radiolysis of water, CO, and CO_2:

\[ \text{H}_2\text{O}(s) \rightarrow \text{O}^*(s) + \text{H}_2^*(s), \]
\[ \text{CO}(s) \rightarrow \text{C}^*(s) + \text{O}^*(s), \]
\[ \text{CO}_2(s) \rightarrow \text{CO}^*(s) + \text{O}^*(s). \]  

\[ \text{CO}_2(s) \rightarrow \text{CO}^*(s) + \text{O}^*(s). \]  

As shown in Figure 4(a), the peak gas-phase relative abundance of NO_2 in our TMC-1 model is \( \sim 4 \times 10^{-11} \), corresponding to a column density of \( \sim 4 \times 10^{11} \text{ cm}^{-2} \). Though this is slightly higher than the predicted abundance of HOCO, observations of NO_2 are challenging due to its small permanent dipole of <1 Debye (Johnson 2016).

4.3. HC_2O

The ketenyl radical, HC_2O, was first observed in the cold \( (T_{\text{kin}} \approx 15 \text{ K}) \) starless cores Lupus-1A and L483 by Agúndez et al. (2015), who derived a column density of \( \sim 5 \times 10^{11} \text{ cm}^{-2} \) for both sources. Chemical simulations were run assuming HC_2O formation via the reaction of OH and C_2H. It was noted that such simulations underproduce the ketenyl radical by about six orders of magnitude, leading the authors to posit the existence of “a powerful formation mechanism” to counterbalance HC_2O destruction pathways.

As shown in Figure 5, the inclusion of radiation chemistry in our TMC-1 simulations results in significant enhancements of HC_2O—roughly four orders of magnitude for the gas, ice surface, and ice bulk. At early simulation times (<10^3 years),
the dominant formation route for gas-phase ketenyl radical is
\[
\text{OH}^+ + \text{CCH} \rightarrow \text{HC}_2\text{O} + \text{H}(g).
\]
(34)
At all later simulation times (>10^3 years), \text{HC}_2\text{O} is mainly formed via
\[
\text{H}(s) + \text{CCO}(s) \rightarrow \text{HC}_2\text{O}(g).
\]
(35)
In both TMC-1 simulations with and without radiation chemistry, there is little difference in the \text{CCH} abundance at all times and for all phases of the model; however, the ice surface and bulk abundances of \text{CCO} are enhanced via the reaction
\[
\text{C}^+(s) + \text{CO}(s) \rightarrow \text{CCO}(s),
\]
(36)
where the suprathermal carbon atoms are formed mainly via the radiolysis of CO.

Though our simulations still underproduce gas-phase \text{HC}_2\text{O} compared with observed values of Agúndez et al. (2015), the significant enhancements seen in models run with radiation chemistry suggest that perhaps radiation chemistry is their speculated powerful formation mechanism. Since we have not included any nonthermal desorption mechanisms caused by the direct cosmic-ray bombardment of dust grains, such as sputtering, it may be that the impact of radiation chemistry on gas-phase abundances is greater than what is implied by our results here.

### 4.4. HCOOCH\(_3\)

As with the other species highlighted thus far, the abundance of methyl formate (HCOOCH\(_3\)) is enhanced in all three phases of the model. In simulations including radiation chemistry, the main production pathways for gas-phase methyl formate are
\[
\text{HCO}^+(s) + \text{CH}_3\text{O}(s) \rightarrow \text{HCOOCH}_3(g)
\]
(37)
and
\[
\text{HCO}(s) + \text{CH}_3\text{O}^+(s) \rightarrow \text{HCOOCH}_3(g).
\]
(38)
Here, the suprathermal HCO is produced mainly via the Type I radiolysis of formaldehyde:
\[
\text{H}_2\text{CO}(s) \rightarrow \text{H}^+(s) + \text{HCO}(s)
\]
(39)
and the methoxy radical is produced from the Type I decomposition of methanol:

\[
\text{CH}_3\text{OH}(s) \rightarrow \text{H}^4(s) + \text{CH}_3\text{O}^4(s).
\]  

(40)

Methyl formate has been a focus of several recent studies that likewise examined its formation in cold cores (Vasyunin & Herbst 2013; Balucani et al. 2015; Chang & Herbst 2016). In Balucani et al. (2015), gas-phase production via

\[
\text{O} + \text{CH}_3\text{OCH}_2 \rightarrow \text{HCOOCH}_3 + \text{H}
\]  

(41)

was considered. As shown in Figure 6, our models predict a peak gas-phase relative abundance of \(\sim 3 \times 10^{-11}\) for methyl formate. Our peak value here is \(\sim 500\%\) larger than the \(\sim 5 \times 10^{-12}\) obtained by Balucani and coworkers in models where they used the standard chemical desorption fraction of 1\%, the efficiency we assume throughout this work. Similarly, Chang & Herbst (2016) achieved somewhat higher gas-phase abundances of methyl formate in a number of their cold core simulations; however, they found that such results required both an enhanced chemical desorption fraction of 10\% and the addition of a novel “chain reaction mechanism” that is not easily implemented in the macroscopic model we have utilized.

Though the number of grain-surface formation routes for COMs like methyl formate are limited in our network—compared with those used in hot core simulations (Garrod et al. 2017)—these results suggest that radiation-chemical reactions may be able to drive the formation of COMs even under cold core conditions. As shown, the production of these complex species is possible because of the suprathermal reactants which form as a result of the radiolytic dissociation of molecules in dust grain ice mantles.

### 4.5. CH\(_3\)CH\(_2\)OH

Unlike the other species highlighted thus far, surface and bulk abundances of the COM, ethanol, were not significantly enhanced in our simulations, including radiation chemistry. However, as shown in Figure 7, the gas-phase abundance is enhanced by ca. an order of magnitude by the Class 2 insertion reaction

\[
\text{CH}_2^2(s) + \text{CH}_3\text{OH}(s) \rightarrow \text{CH}_3\text{CH}_2\text{OH}(g).
\]  

(42)
This insertion reaction, which was recently studied experimentally by Bergantini et al. (2018), was shown to efficiently form both ethanol—as well as dimethyl ether—in low-temperature ices. In that work, Bergantini and coworkers found that CH$_2^*$ was formed from the radiolytic decomposition of methane:

$$\text{CH}_4(s) \rightarrow \text{CH}_2^*(s) + \text{H}_2(s).$$ \hspace{1cm} (43)

This process, which we have included in our network, is the dominant formation route of CH$_2^*$ at all model times. The results shown in Figure 7 highlight the effect that Class 2 reactions such as insertions can have on the production of COMs in cold sources. Again, we note that since chemical desorption at the standard 1% efficiency is the dominant nonthermal desorption mechanism in our model, the influence of reaction (42), and similar surface reactions, is likely underestimated here.

4.6. Results Using Enhanced Ionization Rates

Additional simulations were run in order to examine the effect of the new radiation chemistry at high $\zeta$. As mentioned in Section 2—and shown in Table 1—we assume that the simulated hypothetical sources are physically identical to TMC-1 except for having higher ionization rates. The results from these model runs for HOCCO, NO$_2$, HC$_2$O, and
HCOOCH$_3$ are depicted in Figures 8–10, which show the gas, surface, and bulk abundances, respectively.

As one can see from a comparison of Figures 8–10, several trends emerge as the ionization rate changes. First, since, as previously demonstrated, the abundances of HOCO, NO$_2$, HC$_2$O, and HCOOCH$_3$ are enhanced due to radiochemical processes, it is reasonable that their abundances should tend to increase with increasing $\zeta$. This effect is most obvious at very early times before $\sim 10^3$ years, with the correlation between the two clearly observable in Figures 8–10. At intermediate times, however, between $\sim 10^3$ and $10^6$ years, the relationship between abundance and $\zeta$ begins to break down, particularly in the gas phase. Generally, we find that the higher the ionization rate, the faster the peak abundance is reached, and the lower the peak value—a trend that can most easily be seen in Figures 9 and 10, which show the surface and bulk abundances, respectively. After $\sim 10^6$ years, an anticorrelation between $\zeta$ and abundance emerges for most of the species shown. The reasons for this behavior are complex, but are driven in part by (a) the increased radiolytic destruction of surface and bulk species into more weakly bound fragments and (b) the greatly increased gas-phase abundances of ions such as H$^+$ and C$^+$ reactions, which further reduce the abundance of the neutral species considered here.

5. Conclusions

We have utilized the theory described in Shingledecker & Herbst (2018) in an initial attempt to incorporate radiation chemistry into an existing chemical network. Simulations of the cold core TMC-1 were run, both with and without the new cosmic-ray-induced reactions. We also modeled several hypothetical sources that were physically identical to TMC-1 aside from having enhanced ionization rates. The major results of the simulations described in this work are the following:

1. Radiation chemistry can result in substantially enhanced abundances in all three model phases for a variety of species, including COMs.
2. These enhancements in abundance occur mainly as a result of reactions involving suprathermal species formed from the radiolytic dissociation of simple ice-mantle constituents.
3. Even under cold core conditions, these suprathermal species can react quickly by a variety of mechanisms,
including insertion, which we found to be particularly important in increasing the abundance of COMs.

4. We predict that HOCO, and perhaps NO₂, could be observable in TMC-1, given a sufficiently deep search.

5. The addition of radiation chemistry substantially improves the agreement between calculated and observed abundances of HC₂O.

6. For the neutral species considered here, ionization rates of \(10^{-16} \text{s}^{-1}\) or higher generally resulted in reduced abundances in all model phases at times greater than \(~10^3\) years.

It should be emphasized that these results, while promising, are necessarily preliminary in nature, given the novelty of incorporating radiation chemistry into astrochemical models. More work is needed to better characterize both (a) cosmic-ray-induced radiolysis and chemistry and (b) secondary effects such as the nonthermal desorption of grain species triggered by cosmic-ray bombardment. These nonthermal desorption mechanisms, such as sputtering, desorption induced by electronic transitions, electron stimulated ion desorption, and Auger stimulated ion desorption (Ribeiro et al. 2015) are particularly promising since they could provide a means of enriching gas-phase abundances at low temperatures, and are therefore a natural complement to the nonthermal chemistry described here.

As we have demonstrated in this work, the addition of cosmic-ray-driven solid-phase reactions can improve existing astrochemical models in a number of significant ways. First, the addition of this nonthermal chemistry increases the realism of models, since cosmic-ray bombardment of ice mantles certainly occurs in the ISM. Moreover, a consideration of solid-phase radiation chemistry both helps to explain how COMs like methyl formate could efficiently form in cold cores (Vasyunin & Herbst 2013; Balucani et al. 2015; Chang & Herbst 2016), and improves the agreement between calculated and observational abundances for HC₂O. Cosmic-ray-driven ice chemistry is thus attractive as a component of future astrochemical modeling studies.

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Figure 10. Calculated bulk-ice abundances of (a) HOCO, (b) NO2, (c) HC2O, and (d) HCOOCH3 calculated at ionization rates of $10^{-17}$ s$^{-1}$ (solid line), $10^{-16}$ s$^{-1}$ (dotted line), $10^{-15}$ s$^{-1}$ (dashed line), and $10^{-14}$ s$^{-1}$ (dotted-dashed line).

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