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Simulations of branched carbon-chain chemistry in star-forming regions

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Abstract. The detection of *iso*-propyl cyanide (i-C_3H_7CN) toward the Galactic Center hot-core source Sgr B2(N) (by Belloche *et al.* 2014) marked the first interstellar detection of an aliphatic molecule with a branched carbon-chain structure. Surprisingly, this branched form was found to have an almost equal abundance with its straight-chain homologue, normal-propyl cyanide (i:n $= 0.40 \pm 0.06$). The detection of this first example of an interstellar molecule with a side-chain raises the question as to how prominent such structures may be in interstellar chemistry, and whether the large branched-to-straight chain ratio is maintained for even larger molecules.

Here are presented recently published models that simulate the chemistry occurring in Sgr B2(N) using a chemical network that explicitly includes the straight-chain and branched forms of propyl cyanide (*normal*/*iso*) and butyl cyanide (*normal*/*iso*/*sec*/*tert*), as well as butane (n/i) and pentane (n/i/*neo*). Formation is assumed to occur on dust-grain surfaces, but a full complement of destruction mechanisms is included both on the grains and in the gas phase.

The models suggest that branched structures become increasingly dominant as molecular sizes increase. In the case of butyl cyanide, the *sec* form is at least ∼2 times more abundant than the straight-chain *normal* form, and together the branched forms dominate *normal*-butyl cyanide by a factor of at least 3. The results for the larger alkanes suggest similarly large ratios of branched to straight-chain molecules. A key set of reactions in the surface/ice chemistry of interstellar nitriles is found to be the addition of the CN radical to unsaturated hydrocarbons, especially acetylene and ethene. The models also predict that the dominant, *sec* form of butyl cyanide reaches a peak abundance equal to that of n-propyl cyanide, albeit with a smaller emission radius. This makes s-C_4H_9CN a good candidate for detection. New ALMA observations to search for this molecule are ongoing.

Keywords. astrochemistry, ISM: abundances, ISM: individual (Sagittarius B2N), ISM: molecules, molecular processes

1. Introduction

Up to now, close to 200 different molecules have been detected in interstellar or circumstellar regions, with many of these containing multiple carbon atoms. However, until recently, almost all such species fell into two groupings: either cyclic molecules (both aromatic and aliphatic), of which relatively few have been detected, with C_{60} and C_{70} being the largest so far (Cami *et al.* 2010); or straight-chain molecules, for example propylene (C_3H_6; Marcelino *et al.* 2007). The latter grouping includes molecules that are actually linear, such as the cyanopolyynes, of which cyanoacetylene (HC_3N) is the simplest; but the underlying structure of most straight-chain organics consists simply of an open, unbranched chain of carbon atoms.

One of the largest unbranched carbon-chain molecules found in the ISM is *normal* propyl cyanide (n-C_3H_7CN), which was detected toward the Galactic Center hot-core region Sgr B2(N) (Belloche *et al.* 2009). Its branched carbon-chain isomer, *iso*-propyl

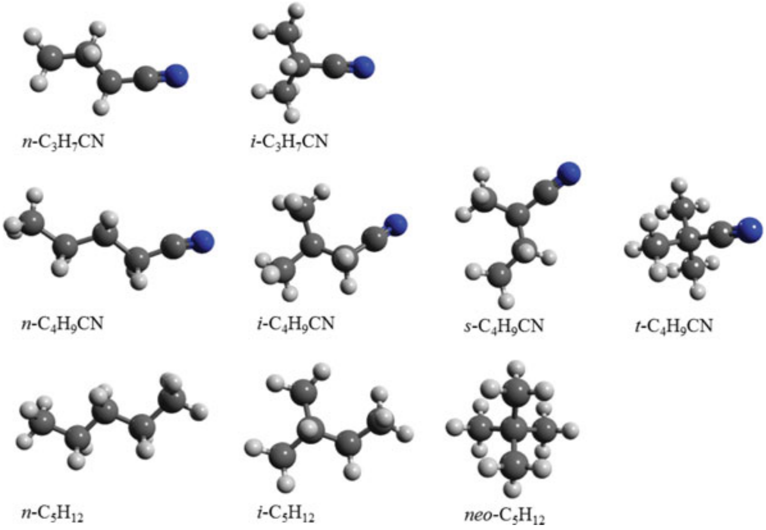

Figure 1. The structures of the various forms of propyl cyanide, butyl cyanide and pentane. Each of these molecules is explicitly considered in the chemical models presented by Garrod *et al.* (2017). *Image credit: Eric Willis*

cyanide (i-C_3H_7CN) was recently detected with the ALMA telescope toward the same source, as part of the *EMoCA* 3-mm line survey of Sgr B2(N) (Belloche *et al.* 2014). This was the first detection of a branched carbon-chain molecule in the ISM. The structures of both forms of propyl cyanide are illustrated in Fig. 1.

The formation of branched structures naturally requires at least four carbon atoms to be present, meaning that a significant degree of chemical complexity must be achieved in the source for branching to arise as an observable feature. Intriguingly, the observed ratio between branched and straight-chain propyl cyanide in Sgr B2(N) is close to unity, at a value $[i{:}n]$=0.40 ± 0.06.

As well as observing propyl cyanide emision, Belloche *et al.* (2014) used the chemical kinetics model *MAGICKAL* (Garrod 2013) to investigate the production of both forms of propyl cyanide in Sgr B2(N) – this itself constituted the first attempt to model branched carbon-chain chemistry in the ISM. It was assumed in this model that, as with many other complex organics, propyl cyanide could be formed on dust grains during the warm-up of the hot core from ∼10 K to the hundreds of Kelvin achieved in hot cores (Garrod & Herbst 2006), to then desorb into the gas phase at yet higher temperatures. In that model, propyl cyanide was produced within or upon the ice mantles that formed on the grains at low temperatures (∼10 K), through the addition of radicals such as CN and C_3H_7, which meet via thermal diffusion at somewhat higher temperatures (>20 K). In order to treat explicitly the formation of the different forms of propyl cyanide, the structures of the pre-cursor radicals and the position of the radical site (i.e. an unpaired electron) also were distinguished. For example, C_3H_7 may take two forms; a primary radical form, where the unparied electron is on an end carbon, and a secondary form, where it is on the middle carbon atom. The addition of the CN radical to either form of C_3H_7 would then produce the corresponding straight-chain or branched form of propyl cyanide. Other formation mechanisms were also included, such as the addition of a methyl group to one or other of the C_2H_4CN radicals, or the addition of radicals C_2H_5 and CH_2CN.

The production mechanisms of pre-cursor radicals on grains and their resultant ratios are critical to the $i{:}n$ ratio achieved for propyl cyanide in the Belloche *et al.* (2013) model.

Table 1. Reactions incorporated into the model of Garrod *et al.* (2017) for the formation of propyl cyanide and butyl cyanide.

CH_3	+	CH_2CH_2CN	→	n-C_3H_7CN
CH_2CH_3	+	CH_2CN	→	n-C_3H_7CN
$CH_2CH_2CH_3$	+	CN	→	n-C_3H_7CN
CH_2	+	CH_2CH_2CN	→	$CH_2CH_2CH_2CN$
H	+	$CH_2CH_2CH_2CN$	→	n-C_3H_7CN
CN	+	C_3H_6	→	CH_3CHCH_2CN
H	+	CH_3CHCH_2CN	→	n-C_3H_7CN
H	+	CH_3CH_2CHCN	→	n-C_3H_7CN
CH_3	+	CH_3CHCN	→	i-C_3H_7CN
CH_3CHCH_3	+	CN	→	i-C_3H_7CN
CH_2	+	CH_3CHCN	→	$CH_2CH(CH_3)CN$
H	+	$CH_2CH(CH_3)CN$	→	i-C_3H_7CN
H	+	$CH_3C(CH_3)CN$	→	i-C_3H_7CN
CH_3	+	$CH_2CH_2CH_2CN$	→	n-C_4H_9CN
CH_2CH_3	+	CH_2CH_2CN	→	n-C_4H_9CN
$CH_2CH_2CH_3$	+	CH_2CN	→	n-C_4H_9CN
$CH_2CH_2CH_2CH_3$	+	CN	→	n-C_4H_9CN
CN	+	C_4H_8	→	$CH_3CH_2CHCH_2CN$
H	+	$CH_3CH_2CHCH_2CN$	→	n-C_4H_9CN
CH_3	+	CH_3CHCH_2CN	→	i-C_4H_9CN
CH_3CHCH_3	+	CH_2CN	→	i-C_4H_9CN
$CH_2CH(CH_3)CH_3$	+	CN	→	i-C_4H_9CN
CH_3	+	CH_3CH_2CHCN	→	s-C_4H_9CN
CH_3	+	$CH_2CH(CH_3)CN$	→	s-C_4H_9CN
CH_2CH_3	+	CH_3CHCN	→	s-C_4H_9CN
$CH_3CHCH_2CH_3$	+	CN	→	s-C_4H_9CN
CH_3	+	$CH_3C(CH_3)CN$	→	t-C_4H_9CN
$CH_3C(CH_3)CH_3$	+	CN	→	t-C_4H_9CN

The mechanisms included for pertinent radicals consist of (i) the direct photodissociation of stable molecules by UV photons induced by cosmic-ray collisions with gas-phase H_2; (ii) the addition of a hydrogen atom to a carbon double- or triple-bond; and (iii) the abstraction of a hydrogen atom from a stable molecule by another radical, often OH or NH_2, which are derived from the major ice components H_2O and NH_3 and which have relatively low barriers to hydrogen abstraction from many other species.

The Belloche *et al.* (2013) model indicated that, with radical production determined as above, the strong bias – especially through pathways (ii) and (iii) – to produce secondary radicals, which are energetically favored, meant that the slight dominance of the straight-chain form of propyl cyanide in the observations could not be reproduced. Indeed, the closest that could be reached was a ratio of ∼2:1 in favor of i-C_3H_7CN. The only mechanism that was effective in producing the *normal* form in any significant quantity was the reaction $C_2H_5 + CH_2CN \rightarrow n\text{-}C_3H_7CN$, which involves radicals for which only a primary form is available, and which therefore has no analog that would allow production of the branched form.

2. Chemical modeling of butyl cyanide

The above-described model by Belloche *et al.* (2014) included propyl cyanide and butane as the only branched species. In order to expand the treatment of branched interstellar molecules, Garrod *et al.* (2017) constructed a larger chemical network that included the next homolog in the series of nitriles, namely butyl cyanide, as well as the equivalent alkane, pentane. Butyl cyanide (C_4H_9CN) contains five carbon atoms, and may exist in one of four forms (*normal*, *sec*, *iso*, and *tert*), illustrated in Fig. 1. Pentane may take three forms (*normal*, *iso*, and *neo*).

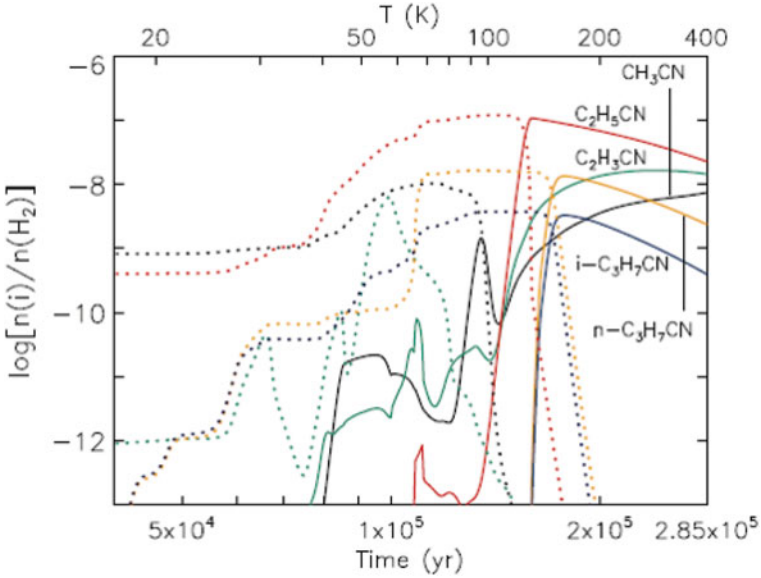

Figure 2. Time- and temperature-dependent chemical abundances for a selection of nitriles during the warm-up of a model hot core, taken from Garrod *et al.* (2017).

As well as including various mechanisms that produce all the possible pre-cursor radicals for the grain-surface/ice formation of butyl cyanide and pentane (as well as gas-phase and grain-surface destruction mechanisms for all new species), another type of reaction was included that was not previously present in the surface chemistry: the addition of the CN radical to species with a carbon double- or triple-bond, producing a radical in which the cyanide group is attached to the terminal carbon in the molecule, leaving a secondary radical that can form a stable, straight-chain molecule by the addition of a hydrogen atom. It was found by Gannon *et al.* (2007) that such processes can occur in the gas phase with no substantial activation energy barrier. The Garrod *et al.* (2017) model assumed that the barriers would be the same for surface/mantle reactions. The full set of reactions included in the model that lead to the various forms of propyl and butyl cyanide are shown in Table 1. All the reactions shown are assumed to have no activation energy barriers.

3. Model results

The inclusion of the above mechanisms for CN to attack carbon multiple bonds allows an appropriate $[i{:}n]$ ratio to be achieved. While the C_2H_5 + CH_2CN reaction is still important, the addition of CN to propylene, followed by the addition of a hydrogen atom to the resulting radical, allows yet more n-C_3H_7CN to be formed. The results for an "intermediate" warm-up timescale (corresponding to a time period of 2×10^5 yr to go from 10–200 K) are shown in Fig. 2; the plot shows the progression of fractional abundances with respect to H_2 over time, during the warm up stage, with dotted lines indicating mantle abundances and solid lines of the same color indicating the gas-phase abundance of the same species. The branched form of propyl cyanide, i-C_3H_7CN, is found to be formed predominantly by the hydrogenation of vinyl cyanide (C_2H_3CN), preferentially forming a secondary radical to which a methyl group (CH_3) can then attach. The *iso* to *normal* ratio for propyl cyanide achieved in the specific model shown, achieved at the time of peak propyl cyanide abundance, is $[i{:}n] = 0.24$.

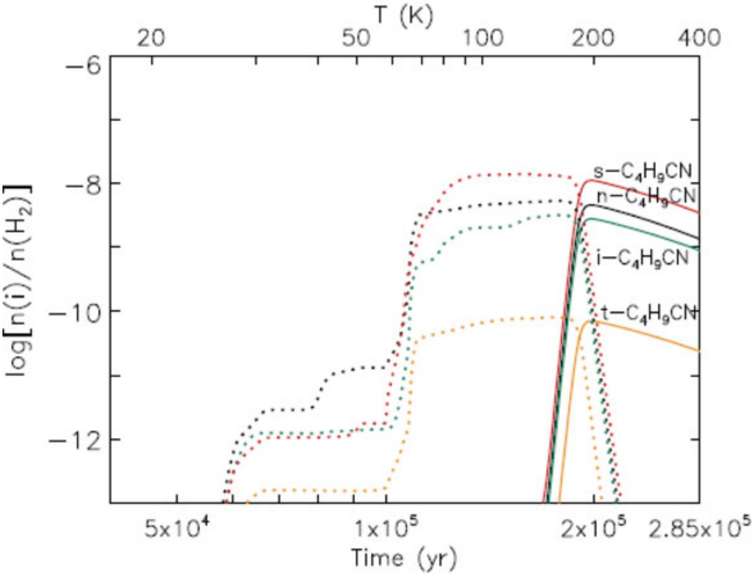

Figure 3. Time- and temperature-dependent chemical abundances for the various forms of butyl cyanide during the warm-up of a model hot core, taken from Garrod *et al.* (2017).

The results for butyl cyanide are shown in Fig. 3. The most abundant forms of butyl cyanide are found to be *sec* and *normal*, in that order; these are produced through a similar mechanism to *iso*-propyl cyanide, i.e. the hydrogenation of vinyl cyanide to either a primary or a secondary radical, followed by the addition of an ethyl group (C_2H_5), forming either the *normal* or *sec* form, respectively. The *sec* form is seen to be ~2 times more abundant than the *normal*. The *iso* form is marginally less abundant than the *normal*, by around a factor of 2, although the range of models by Garrod *et al.* (2017) generally produce a ratio of around unity. The *tert* form, however, is never very abundant, and is therefore unlikely to be detected easily. Summing the abundances of all branched molecules gives a ratio $[(i{+}s{+}t){:}n] = 3$, which is the lowest value achieved in the several model runs tested by Garrod *et al.* (2017), with others producing values as high as 5.8.

It is found that, for the alkanes (see Fig. 4), *normal*-butane strongly dominates the branched *iso* form, whereas *iso*-pentane dominates over *normal*-pentane. *Neo*-pentane, which, like *tert*-butyl cyanide, is doubly branched, is an order of magnitude less abundant that the straight-chain form.

4. Conclusions

Several conclusions may be drawn from the models of propyl and butyl cyanide. The inclusion of reactions in which CN radicals may attack carbon multiple bonds, with no significant activation energy barrier to overcome, allows appropriate quantities of the straight-chain form of propyl cyanide to be produced on dust grains. In general, one might expect that in cases where branched forms of molecules may be produced, they will tend to dominate, due to the propensity to form secondary radicals over primary radicals. The nitriles (and indeed butane) appear to be an exception to this outcome, but only for propyl cyanide; for the next largest homolog, butyl cyanide, the branched forms together dominate, and *sec* in particular is the most abundant form. The *normal* form of butyl cyanide was searched for in the *EMoCA* survey data; no detection was

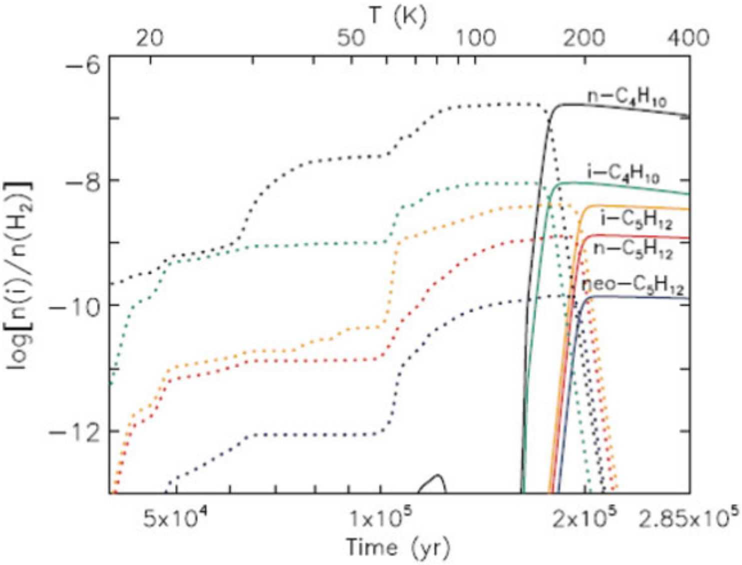

Figure 4. Time- and temperature-dependent chemical abundances for the various forms of butane and pentane during the warm-up of a model hot core, taken from Garrod *et al.* (2017).

forthcoming, but an upper limit ratio with n-propyl cyanide of <0.59 was obtained. This value is consisitent with the range produced by the models of $\sim 0.1 - 1$.

Sec butyl cyanide is predicted to be the most abundant form of this molecules, and may be detectable as a result; the n and i forms are also plausible detection targets, but the abundance of t-C_4H_9CN predicted in the models makes it a poor candidate for detection. Observational efforts to detect the former three forms are ongoing.

It should be noted that vinyl cyanide (C_2H_3CN) appears to be important to the formation of larger nitriles, as it may be hydrogenated to produce radicals (both primary and secondary) to which methyl and ethyl groups can attach. In fact, almost all of the grain surface-produced vinyl cyanide in the models is converted to another larger nitrile (mainly ethyl cyanide, C_2H_5CN). The gas-phase vinyl cyanide that peaks at high temperatures is actually formed through the destruction of gas-phase ethyl cyanide, following its desorption from grains.

The models presented here show that branching in organic molecules is likely to be an important feature in interstellar chemistry, especially in star-forming regions, where the degree of observable chemical complexity is usually greatest.

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