

CALCULATIONS CONCERNING INTERSTELLAR ISOMERIC ABUNDANCE RATIOS FOR C_3H AND C_3H_2

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ABSTRACT

The syntheses of interstellar c - C_3H_2 , H_2CCC , c - C_3H , and HCCC, where “ c ” stands for the cyclic isomer, are thought to proceed via dissociative recombination of the precursor ions c - $C_3H_3^+$ and H_2CCCH^+ , which are themselves produced mainly via the radiative association reaction between C_3H^+ and H_2 . We have utilized ab initio methods to study the potential energy surface (PES) for the association of the linear ion C_3H^+ and H_2 to form the isomers c - $C_3H_3^+$ and H_2CCCH^+ . The overall rate coefficient for radiative association has been calculated as a function of temperature via the phase space method. Our ab initio calculations show that the H_2CCCH^+ isomer is formed directly without an activation barrier from reactants, and that isomerization between the two isomers can occur readily via a low-energy pathway consisting of two transition states (saddle points on the PES) and one intermediate (local minimum on the PES). Calculation of the equilibrium coefficient for the isomerization $H_2CCCH^+ \rightleftharpoons c$ - $C_3H_3^+$ as a function of energy shows that equal abundances of these two ions should be produced as relaxation proceeds, in agreement with experimental measurements at high pressure. *Our results confirm the important point that a simple ion-molecule association reaction can produce a cyclic hydrocarbon.* If dissociative recombination reactions involving c - $C_3H_3^+$ and H_2CCCH^+ maintain the carbon skeletal structure of the ions and produce roughly similar C_3H/C_3H_2 branching ratios, then abundance ratios of unity are produced between the cyclic and noncyclic isomers of C_3H and C_3H_2 via this mechanism. The large abundance ratio of c - C_3H_2 to H_2CCC observed in TMC-1 can then be explained by differential destruction rates.

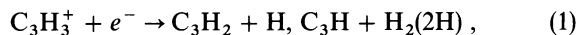
Subject headings: ISM: molecules — molecular processes

1. INTRODUCTION

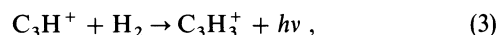
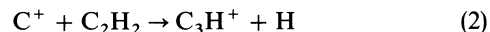
The list of interstellar molecules with more than one isomeric form continues to grow. Although stable molecules such as ethanol (C_2H_5OH) and dimethyl ether (CH_3OCH_3) are included in the list, it is noteworthy that many reactive species have also been detected, as had been predicted quite some time ago by Green & Herbst (1979) via general ion-molecule arguments. Most recently, assorted isomers of HC_3N have been detected (Kawaguchi et al. 1992a, b). Perhaps the most interesting isomeric pairs of species seen in the interstellar medium belong to the unsaturated three-carbon-atom hydrocarbons C_3H_2 and C_3H . Both of these molecules have been detected in a triangular, or cyclic (“ c ”) form, and a noncyclic form with a linear carbon skeleton. The cyclic form of C_3H_2 , termed “cyclopropenylidene,” is a widespread interstellar molecule. Originally detected by Thaddeus, Vrtilek, & Gottlieb (1985b) based on their own laboratory work, it has also been studied by Matthews & Irvine (1985) and others. Recently, the cumulene or carbene form of this species, H_2CCC (propadienylidene), has been detected by Cernicharo et al. (1991) in TMC-1 based on laboratory work of Vrtilek et al. (1990). This form is calculated to lie 0.63 eV higher in energy than c - C_3H_2 (DeFrees & McLean 1986). The observed abundance of c - C_3H_2 in TMC-1 far exceeds that of H_2CCC ; the actual abundance ratio c - C_3H_2/H_2CCC is 70. Unlike the case of C_3H_2 , the

cyclic form of C_3H is calculated to lie higher (≈ 2.62 eV) in energy than its noncyclic counterpart (Baker et al. 1989). The linear form of this species was detected in the interstellar medium first (Thaddeus et al. 1985a; Gottlieb et al. 1985). The subsequent detection of the cyclic isomer in TMC-1 was made by Yamamoto et al. (1987) and showed the c - $C_3H/HCCC$ abundance ratio in TMC-1 to be near unity (Saito 1990).

The ion-molecule synthesis of these three-carbon-atom hydrocarbons is thought to proceed via dissociative recombination of the precursor ion $C_3H_3^+$ (Herbst, Adams, & Smith 1984; Adams & Smith 1987):



although the product branching ratios have still not been measured. The $C_3H_3^+$ ion is in turn thought to be produced mainly via the reactions (Herbst et al. 1984; Adams & Smith 1987)



which produce and destroy the linear ion C_3H^+ . The $C_3H_3^+$ ion is known to have two isomeric forms—a cyclic one and one with a linear carbon skeleton (H_2CCCH^+)—with the cyclic one somewhat lower in energy (Lias et al. 1988). If the assumptions are made that dissociative recombination with electrons is the dominant depletion mechanism and that it does not disturb the carbon skeletal structure of the parent ions, then the isomeric composition of the product of reaction (3) determines the relative production rates of the cyclic and noncyclic forms of the neutral C_3H_n ($n = 1, 2$) products. At least one additional assumption, concerning the branching ratios between the $n = 1$ and $n = 2$ hydrocarbons for both c - $C_3H_3^+ + e^-$ and $H_2CCCH^+ + e^-$, is needed to complete the analysis

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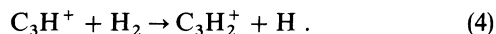
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of the relative production rates of cyclic and noncyclic forms of C_3H and C_3H_2 . Thus, an understanding of reaction (3), while necessary, is only an initial step toward a complete understanding of the production rates of $c\text{-}C_3H$, $c\text{-}C_3H_2$, HCCC, and H_2CCC .

An attempt to measure the isomeric branching ratio for the product of the association of $C_3H^+ + H_2$ was made by Smith & Adams (1987) and Adams & Smith (1987) who found under high-density conditions, when the association to form stable $C_3H_3^+$ occurs via collisional (ternary) rather than radiative stabilization, that the $c\text{-}C_3H_3^+$ and H_2CCCH^+ isomers are produced in nearly equal abundance, independent of temperature. This initially surprising result implies that the system is able to undergo a profound structural change from a linear to a cyclic carbon skeleton. Based on an unusual saturation pattern for the ternary association, Smith & Adams (1987) conceived the mechanism of the association reaction to be one in which the reactants first form a weakly bound, long-range complex, which then isomerizes to the $c\text{-}C_3H_3^+$ ion. This ion can then be stabilized in its cyclic form, or equilibrate in some manner with the H_2CCCH^+ form. Another exit channel measured was dissociation of the reaction complex into $C_3H_2^+ + H$ products:



The weakness of this channel at low temperatures indicated to Smith & Adams (1987) that it was slightly endothermic, by perhaps 1 kcal mol^{-1} , and therefore of no importance at interstellar temperatures unless the reactant ion is translationally excited (Herbst et al. 1984; Brown, Cragg, & Bettens 1990). However, the reported endothermicity of this channel was disputed by Prodruk, Depuy, & Bierbaum (1990) who found indirectly that the channel is exothermic by 6 kcal mol^{-1} if the ion product is $c\text{-}C_3H_2^+$. Support for the exothermicity of this channel has recently come from Gerlich & Horning (1992) who found the $c\text{-}C_3H_2^+ + H$ channel to dominate over the radiative association channel at 80 K and low gas densities. In particular, at the lowest densities of their experiment, they measured the radiative association rate coefficient for reaction (3) to be $3.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and the ion-molecule reaction rate coefficient for reaction (4) to be $6 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. To explain their results, Gerlich & Horning (1992) adopted a mechanism in which the reactants first form a reaction complex of either "linear" or cyclic geometry, with the linear complex less strongly bound and consequently shorter lived. At low gas densities, the cyclic complex dominates and either is stabilized to form $c\text{-}C_3H_3^+$ or (predominantly) dissociates into $c\text{-}C_3H_2^+$. At higher densities (such as those investigated by Smith & Adams 1987), more frequent collisions manage to stabilize both the cyclic complex as well as the "linear" complex to produce H_2CCCH^+ .

Although there has been some previous theoretical work on the $C_3H_3^+$ potential energy surface (Wong & Radom 1989; Li & Riggs 1992), the lack of a detailed theoretical treatment of the $C_3H^+ + H_2$ reactions and the apparently conflicting results of different experimental investigations have motivated us to study this system via ab initio quantum chemical techniques and dynamical calculations. Many of the details of our investigation are to be found in a parallel publication to be published in the chemical literature (Maluendes et al. 1993). In this paper, we report on those aspects of our work most relevant to interstellar chemistry, in particular the overall rate of reaction (3), the relative rates of production of $c\text{-}C_3H_3^+$ and H_2CCCH^+ in reaction (3), and the exothermicity or endo-

thermicity of the reactive channel (4). A rather speculative discussion on the causes of the differing $c\text{-}C_3H_2/H_2CCC$ and $c\text{-}C_3H/HCCC$ abundance ratios in TMC-1 is also included.

2. QUANTUM CHEMICAL RESULTS

The potential energy surface for the reactions between C_3H^+ and H_2 has been investigated in some detail (Maluendes et al. 1993). Briefly, the stationary points on the reaction pathway have been characterized at the MP2/(5s3pd/3sp) level of theory. Energies for each structure were refined using more sophisticated electron correlation techniques and larger basis sets. The highest level of theory utilized was the so-called QCISD(T) approach (Pople, Head-Gordon, & Raghavachari 1987). The minimum energy potential surface for association to form the two isomers of $C_3H_3^+$ and to form the low-energy ion-molecule products $c\text{-}C_3H_2^+ + H$ obtained at our highest level of calculation is shown in Figure 1, with energies (including zero-point energy contributions at the MP2 level) listed in eV. As can be seen in the figure, the reactants C_3H^+ and H_2 initially form the strongly bound H_2CCCH^+ , or propargyl, ion without any entrance channel barrier. Thus, the mechanism of Smith & Adams (1987), in which only a weakly bound, long-range complex can be formed initially, is incompatible with our calculations. The H_2CCCH^+ cation can isomerize to the lower energy, cyclic form of $C_3H_3^+$ via a pathway in which two transition states and one stable intermediate are accessed (see Fig. 1). The transition states lie at energies significantly below the reactant energy. An earlier calculation by Wong & Radom (1989) found a similar transition state-intermediate-transition state pathway for isomerization, but at considerably higher energies. Thus, the cyclic $C_3H_3^+$ complex cannot be formed directly from reactants but only from the propargyl ion. This "series" picture would seem to conflict with the "parallel" mechanism of Gerlich & Horning (1992), in which the reactants are able to access initially both the cyclic and H_2CCCH^+ isomers. Another pathway for isomerization we have obtained, not shown in Figure 1, occurs via a significantly higher energy transition state (Maluendes et al. 1993). Since the depicted transition states for isomerization of $C_3H_3^+$ themselves lie almost 2 eV below the energy of reactants, there is no hindrance to rapid isomerization between H_2CCCH^+

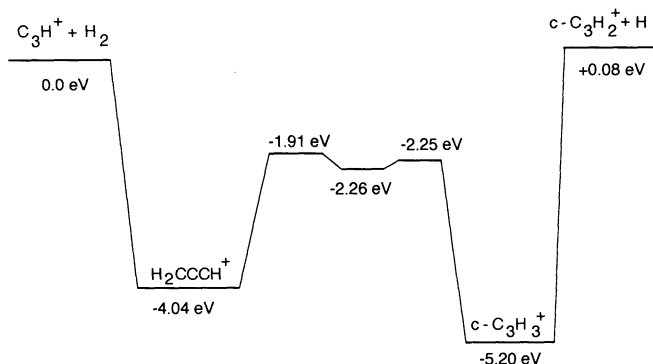


FIG. 1.—The minimum energy potential surface is depicted for the association and product channels of the reactants $C_3H^+ + H_2$. The energies of all stationary points are listed in eV and include zero-point energy corrections as discussed in the text. The linear ion C_3H^+ initially reacts with H_2 to form the propargyl cation H_2CCCH^+ , which possesses a linear carbon skeleton. Isomerization to the lower energy cyclic form $c\text{-}C_3H_3^+$ can occur via a rather convoluted but low-energy pathway. Dissociation of $c\text{-}C_3H_3^+$ into $c\text{-}C_3H_2^+ + H$ is calculated to be endothermic by 0.076 eV or 1.7 kcal mol $^{-1}$.

and $c\text{-C}_3\text{H}_3^+$ when these ions are formed by association of $\text{C}_3\text{H}^+ + \text{H}_2$. Indeed, even protonation of $c\text{-C}_3\text{H}_2$ or H_2CCC by reaction with the ion H_3^+ and other protonating ions can also produce C_3H_3^+ ions above the isomerization barrier. In our calculations, the cyclic isomer of C_3H_3^+ lies $1.16 \text{ eV} = 26.7 \text{ kcal mol}^{-1}$ below the propargyl ion. This compares favorably with the experimental value (Lias et al. 1988) of 25 kcal mol^{-1} .

In addition to the association channel, we have also calculated the energy of the channel $c\text{-C}_3\text{H}_2^+ + \text{H}$. As shown in Figure 1, we calculate this reaction channel to be endothermic by 0.08 eV or $1\text{--}2 \text{ kcal mol}^{-1}$, in excellent agreement with the older experimental work of Smith & Adams (1987) but in disagreement with the work of Prodnuk et al. (1990) and Gerlich & Horning (1992). Although it is difficult to estimate uncertainties in high-quality ab initio results, we believe that our results are not consistent with a reaction that is exothermic by as much as 6 kcal mol^{-1} (Prodnuk et al. 1990). Recent ab initio theoretical work by Wong & Radom (1993) at the G2 level also shows the reaction to be slightly endothermic and has cast further doubt on the result of Prodnuk et al. (1990) by illuminating a probable flaw in their arguments.

3. DYNAMICAL CALCULATIONS

We have previously utilized the phase space approach to calculate the rates of competing association and product channels in systems with more than one potential minimum (Herbst & Yamashita 1993). However, the convoluted nature of the isomerization pathway between the propargyl cation H_2CCCH^+ and $c\text{-C}_3\text{H}_3^+$ cannot readily be treated by phase space methods. We have therefore chosen to calculate the overall association rate between C_3H^+ and H_2 in a seriatum manner. First, the isomerization is assumed to be sufficiently rapid for C_3H_3^+ ions possessing the energy of the $\text{C}_3\text{H}^+ + \text{H}_2$ reactants that an equilibrium can be maintained and the relative abundances of the two isomers obtained from calculation of the equilibrium coefficient. For isomerization to be in equilibrium requires only that the isomerization rates be more rapid than the stabilization/relaxation rates of the cations, which are at most 10^7 s^{-1} in a high-density apparatus. The calculation of the equilibrium coefficient, discussed below, shows that the propargyl ion is favored over the cyclic ion when the system is still at the energy of the reactants. A similar calculation was performed by DeFrees, McLean, & Herbst (1985) for the protonated cyanide and isocyanide ions produced in the association of CH_3^+ and HCN. Second, based on our calculated results for the equilibrium coefficient, we have used phase space theory to calculate the association rate coefficient with the simplifying assumption that the propargyl complex is the only one of the two isomeric complexes we need consider.

The microcanonical equilibrium coefficient K_{eq} relating the abundance of $c\text{-C}_3\text{H}_3^+$ to H_2CCCH^+ at a specific energy E is given by the expression

$$K_{\text{eq}}(E) = \sum_{J=0}^{J_{\text{max}}} (2J+1)^2 \times \left\{ \rho_v(c\text{-C}_3\text{H}_3^+) / \rho_v(\text{H}_2\text{C}_3\text{H}^+) \right\} \left/ \sum_{J=0}^{J_{\text{max}}} (2J+1)^2 \right., \quad (5)$$

where ρ_v is the vibrational-nuclear spin density of states, and the sum is over all angular momenta J up to the maximum allowed by the Langevin model for collisions (Bates & Herbst 1988). The rotational weighting is appropriate for nonlinear complexes in which the K rotational structure is assumed to be

degenerate ("spherical" tops). The vibrational density of states functions are computed via the semiclassical approach of Whitten & Rabinovitch (1963) with rotational energy subtracted from the total energy E . The relative energies, vibrational frequencies, and rotational constants for the two complexes needed in the calculation of $K_{\text{eq}}(E)$ are taken from our ab initio results (Maluendes et al. 1993). A collision energy of 0.001 eV corresponding to a temperature of $\approx 10 \text{ K}$ has been assumed to determine J_{max} . The results are shown in Figure 2, where K_{eq} is plotted versus energy E , with the zero of energy defined as the reactant energy at 0 K . Negative energies refer to complexes that have lost sufficient energy via radiation and/or collisions to lie below the energy of reactants and to therefore be stabilized. Isomerization can still occur at negative energies until, in the absence of tunneling, the system relaxes to an energy of -1.91 eV , which corresponds to the height of the transition state barrier for formation of the intermediate structure in the isomerization.

Figure 2 shows that K_{eq} is less than unity at all feasible energies. At an energy $E = 0$, $K_{\text{eq}} \approx 0.3$, and rapid isomerization leads to a cyclic ion/propargyl ion ratio equal to this value. The propargyl ion is favored despite the fact that it is the higher energy isomer because it possesses a higher density of vibrational-nuclear spin states due to some low-frequency oscillators. As the system relaxes, however, the lower energy isomer begins to become more important. At the lowest energy at which isomerization is possible, K_{eq} has increased to 0.9 , and the cyclic and propargyl isomers reach roughly equal abundances. Since tunneling should allow isomerization to continue to even lower energies before it becomes uncompetitive with respect to relaxation, it is safe to predict that roughly equal abundances of the propargyl and cyclic ions will be formed by the time relaxation is complete, in excellent agreement with the experimental results of Adams & Smith (1987). The result is rather independent of collision energy. The competition between isomerization and relaxation has been discussed in detail by DeFrees et al. (1985).

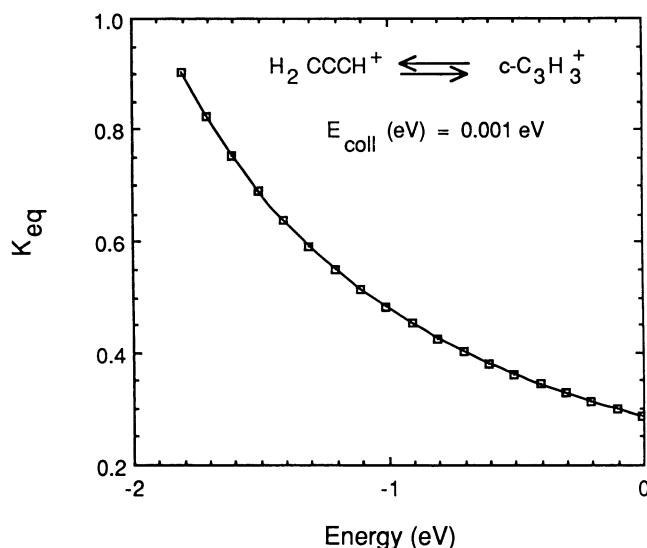


FIG. 2.—The calculated equilibrium coefficient K_{eq} for the isomerization process $\text{H}_2\text{CCCH}^+ \rightleftharpoons c\text{-C}_3\text{H}_3^+$ is plotted vs. the energy (eV) of the system. The zero of energy is defined as the energy of reactants at 0 K ; negative energies refer to a system that has relaxed via radiative emission or collisions. The initial collision energy is 0.001 eV , which refers to collisions at roughly 10 K .

The phase space treatment (Herbst 1987; Herbst & Dunbar 1991; Herbst & Yamashita 1993) has been utilized to determine the rate of the radiative association reaction between $\text{C}_3\text{H}^+ + \text{H}_2$ to form H_2CCCH^+ , without the consideration of isomerization at the collision energy. Specifically, the required density-of-states and geometrical parameters used in the theory are those pertaining to H_2CCCH^+ rather than to $c\text{-C}_3\text{H}_3^+$. As relaxation proceeds, isomerization will drive the system to equilibrium between the two forms of C_3H_3^+ , although this is not formally treated in our phase space calculation. The error incurred in excluding the cyclic isomer in this manner is small compared with other sources of uncertainty. We have assumed that complex formation and redissociation can convert ortho- to para- H_2 and vice versa. This exchange implicitly requires that isomerization occurs between the two forms of C_3H_3^+ because ortho/para exchange requires a reasonably symmetric intermediate in which the hydrogen atoms lose the memory of their formation. The radiative stabilization rate has been set to 500 s^{-1} , in accord with a mechanism in which the emission derives from purely vibrational transitions (Herbst & Dunbar 1991; Gerlich & Horning 1992; Herbst & Yamashita 1993). A suggestion of Gerlich & Horning (1992) that more rapid emission due to electronic transitions is important is ruled out for the cyclic isomer since our ab initio calculations reveal no suitable low-lying electronic states (Maluendes et al. 1993). The results for the radiative association rate coefficient $k_{\text{ra}} (\text{cm}^3 \text{ s}^{-1})$ as a function of temperature in the 10–100 K range are shown in Figure 3 and listed in Table 1. It has been assumed in the calculations that the ortho and para states of hydrogen are in thermal equilibrium. The calculated rate coefficient at 20 K is more than two orders of magnitude larger than a previous estimate (Herbst et al. 1984)! The rate coefficient for normal $-\text{H}_2$ ($\frac{1}{4}$ para, $\frac{3}{4}$ ortho) is calculated to be $8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at 80 K, in very good agreement with a recent experimental value of $3.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (Gerlich & Horning 1992). The experimental results at higher densities, where association is predominantly collisional in nature, are in much poorer agreement with calculation (Maluendes et al. 1993). In addition, the $c\text{-C}_3\text{H}_2^+ + \text{H}$ channel measured at 80 K to be dominant by Gerlich & Horning (1992) does not occur appreciably according to theory due to its endothermicity.

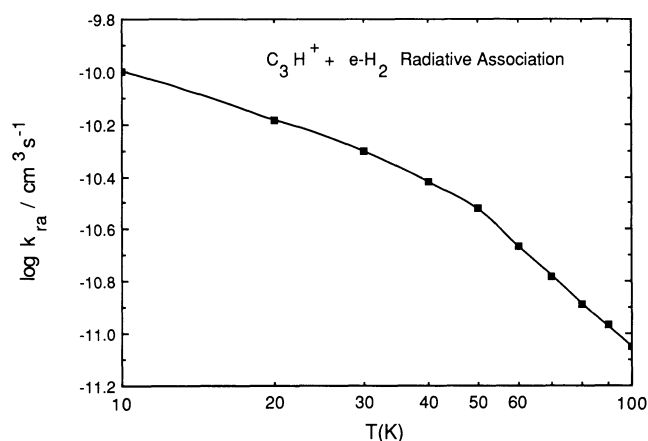


FIG. 3.—The log of the calculated radiative association rate coefficient $k_{\text{ra}} (\text{cm}^3 \text{ s}^{-1})$ for $\text{C}_3\text{H}^+ + \text{H}_2$ in rotational equilibrium is plotted against $T(\text{K})$. The inverse temperature dependence becomes less severe at low temperatures.

TABLE 1

CALCULATED VALUES FOR THE
RADIATIVE ASSOCIATION RATE
COEFFICIENT FOR THE PROCESS
 $\text{C}_3\text{H}^+ + e\text{-H}_2 \rightarrow \text{C}_3\text{H}_3^+$

Temperature (K)	$k_{\text{ra}} (\text{cm}^3 \text{ s}^{-1})^a$
10.....	1.01 (–10)
20.....	6.52 (–11)
30.....	4.96 (–11)
40.....	3.82 (–11)
50.....	3.02 (–11)
60.....	2.16 (–11)
70.....	1.66 (–11)
80.....	1.29 (–11)
90.....	1.08 (–11)
100.....	8.95 (–12)

NOTE.— $a(b)$ means $a \times 10^{-b}$.

^a H_2 is assumed to have its rotational-nuclear spin levels in thermal equilibrium.

4. DISCUSSION

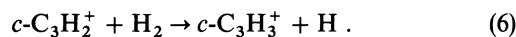
In agreement with the experimental work of Smith & Adams (1987) and Adams & Smith (1987) at high densities, we have determined that the propargyl and cyclic C_3H_3^+ ions produced via the association of $\text{C}_3\text{H}^+ + \text{H}_2$ are formed in roughly equal abundance. With the reasonable assumption that dissociative recombination does not interconvert the cyclic and linear carbon skeletal frameworks, we infer that the $\text{C}_3\text{H}_3^+ - e^-$ decomposition products are divided equally between cyclic and noncyclic structures. Then, if the branching ratio between C_3H and C_3H_2 is similar for both $c\text{-C}_3\text{H}_3^+ - e^-$ and $\text{H}_2\text{CCCH}^+ - e^-$ reactions, both C_3H and C_3H_2 are produced with 1:1 abundance ratios between noncyclic and cyclic isomers, unless the H_2CCCH^+ ion, which is the more reactive of the two C_3H_3^+ structures, is preferentially depleted via ion-molecule reactions, a possibility we and others consider unlikely (Adams & Smith 1987). Yet another complication is that the propargyl ion can dissociatively recombine with electrons to produce noncyclic C_3H_2 neutrals of the nonlinear structure HCCCH . Since such structures are calculated to lie at higher energies than H_2CCC (DeFrees & McLean 1986), phase space theory predicts H_2CCC to be a more likely product (Galloway & Herbst 1991). Ion-molecule protonation reactions will recycle a percentage of the C_3H_2 product molecules through energetic C_3H_3^+ molecules capable of isomerization. This feedback mechanism, termed a “secondary” synthesis by Green & Herbst (1979), is important only if an isomer is not formed appreciably in the primary formation step. Here, the recycled C_3H_3^+ energetic ions simply maintain the 1:1 abundance ratio through isomerization.

Assuming that the $\text{C}_3\text{H}^+ + \text{H}_2$ association reaction is the dominant formation mechanism of C_3H_3^+ , which in turn is the dominant precursor of C_3H and C_3H_2 , we must still consider the relative destruction rates of the C_3H and C_3H_2 isomers to arrive at abundance ratios. If, as argued above, the formation rates of both pairs of isomers are roughly equal, to reproduce the observed abundance ratios in TMC-1 requires (1), that the depletion rates of the cyclic and linear forms of C_3H be roughly the same; and (2), that the depletion rate of H_2CCC exceed that of $c\text{-C}_3\text{H}_2$ by perhaps a factor of 70. A rationalization of these apparently contradictory data is readily forthcoming in terms of neutral-neutral reaction rates. It is important to remember that if a neutral species reacts with abundant atoms, it can be destroyed much more rapidly than if its destruction is

determined by ion-molecule reactions. Consider the following analysis. Assume a typical neutral-neutral reaction rate coefficient to be $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and the overall fractional abundance of reactive atoms to be $\approx 10^{-4}$ (Herbst & Leung 1989). Next, assume a typical ion-molecule rate coefficient for a moderately polar neutral species to be $10^{-8} \text{ cm}^3 \text{ s}^{-1}$ and a fractional ionization for reactive ions to be $\approx 10^{-8}$ (Herbst & Leung 1989). The overall neutral-neutral depletion rate then exceeds the ion-molecule depletion rate by ≈ 1 order of magnitude. When recycling of protonated product ions is taken into account, the differential can become significantly greater.

Both cumulene structures—HCCC and H_2CCC —should be exceedingly reactive with abundant atoms since they possess highly reactive terminal carbon atoms. In the case of C_3H , the cyclic isomer possesses a ground state of $^2\text{B}_2$ symmetry (Saito 1990). Open shell electronic states are also associated with rapid neutral-neutral reactions (Clary, Stoeklin, & Wickham 1993). The case of $c\text{-C}_3\text{H}_2$ is quite different, however. It is a closed-shell, cyclic species; cyclic molecules, even if ionic such as $c\text{-C}_3\text{H}_3^+$, are known for their inert behavior (Adams & Smith 1987). If $c\text{-C}_3\text{H}_2$ can only be depleted via ion-molecule reactions, it will possess a larger abundance than H_2CCC , by perhaps the requisite factor of ≈ 70 to match the abundance ratio detected in TMC-1. This analysis is strengthened by the observation that the abundances of $c\text{-C}_3\text{H}$ and HCCC in TMC-1 lie close to that of H_2CCC .

If our calculations that reaction (4) is endothermic are incorrect, and this reaction dominates association at low temperatures and gas densities, as measured by Gerlich & Horning (1992), then another possibility looms. The only arguably exothermic channel for reaction (4) leads to the cyclic form of C_3H_2^+ . This ion can then react exothermically with H_2 to form $c\text{-C}_3\text{H}_3^+$ (but not H_2CCCH^+):



The reaction has been studied at low temperature (Gerlich & Horning 1992) and proceeds slowly but with a nonzero rate coefficient, due to a small barrier (Wong & Radom 1993). Via this pathway, the cyclic form of C_3H_3^+ is the only isomer produced, and the subsequent dissociative recombination reactions lead to only $c\text{-C}_3\text{H}_2$ and $c\text{-C}_3\text{H}$ if the carbon skeletons are maintained during neutralization. The cumulene forms of the hydrocarbons can then be formed only via “secondary” syntheses, which can lead to lower abundances (Green & Herbst 1979). Although such an explanation helps perhaps to explain the high $c\text{-C}_3\text{H}_2/\text{H}_2\text{CCC}$ abundance ratio seen in TMC-1, it certainly does not help to explain the $c\text{-C}_3\text{H}/\text{HCCC}$ abundance ratio of unity seen in this source.

If reaction (4) is exothermic, and there is no barrier along the dissociation pathway from $c\text{-C}_3\text{H}_3^+$, the branching ratio obtained by Smith & Adams (1987) for reaction (3) is probably incorrect. Even at high density, competition between normal

and association channels appear to be theoretically possible only if there is some barrier in the exit channel which slows down the formation of products (Herbst 1985, 1987) or if the association and ion-molecule product channels occur via totally different “parallel” mechanisms (Herbst & Yamashita 1993; Yamashita & Herbst 1992). Any competition would be between reaction (4) and association to form H_2CCCH^+ , which could possibly occur for high angular momentum collisions in which the barrier separating this ion and products is increased by a centrifugal contribution (Herbst 1987). A theoretical test of this possibility requires detailed calculation of the dissociation rate of propargyl ion complexes which, given the complexity of the potential pathway, is not feasible. We note, however, that previous calculations of competition between association and normal channels due to barriers have dealt with systems in which the neutral reactant is polar, leading to much greater values of collision angular momentum (Herbst 1987).

In conclusion, we have utilized detailed ab initio, quantum chemical methods to follow the minimum energy pathway for both the associative and reactive channels of the reactants $\text{C}_3\text{H}^+ + \text{H}_2$. We have found that isomerization between the two forms of C_3H_3^+ formed during the course of the reactions is unhindered by any energy barrier, and that, as C_3H_3^+ relaxes via collisions and/or emission of radiation, it tends to form roughly equal abundances of the cyclic and propargyl isomers, in agreement with experiment (Adams & Smith 1987), if isomerization is sufficiently rapid. The ion-molecule reaction to form $c\text{-C}_3\text{H}_2^+$ is calculated to be $1\text{--}2 \text{ kcal mol}^{-1}$ endothermic, in agreement with a theoretical study (Wong & Radom 1993) and with some experimental studies (Smith & Adams 1987; Adams & Smith 1987), but in disagreement with other experimental studies (Prodruk et al. 1990; Gerlich & Horning 1992). If interstellar $c\text{-C}_3\text{H}$, HCCC, $c\text{-C}_3\text{H}_2$, and H_2CCC are formed primarily through energetic $c\text{-C}_3\text{H}_3^+$ and H_2CCCH^+ ions, and if subsequent dissociative recombination reactions both preserve the carbon skeletal structures and possess similar branching ratios between the C_3H and C_3H_2 products, theory suggests that the cyclic and cumulene forms of C_3H and C_3H_2 are produced in roughly equal abundance. Any strong deviations from this abundance ratio are best blamed on differing depletion rates, although a wealth of additional data on dissociative recombination reaction branching ratios and neutral atom- C_3H_n reaction pathways is needed to test this assertion.

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