

THEORETICAL REINVESTIGATION OF HYDROCARBON AND  
CYANOACETYLENE ABUNDANCES IN TMC-1

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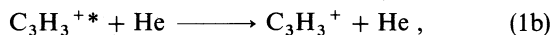
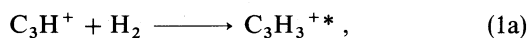
## ABSTRACT

The products of the reaction between  $C_3H^+$  and  $H_2$  at low temperatures were previously reported incorrectly by us to be  $C_3H_2^+ + H$ . The only product at 80 K (and presumably at lower temperatures) is  $C_3H_3^+$ , formed via a saturated three-body association reaction. Use of the analogous radiative association reaction with a rate coefficient of  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$  as well as a newly measured rate coefficient for the radiative association reaction between  $CH_3^+$  and  $H_2$  in Herbst's "semidetached" model of the dense interstellar cloud TMC-1 results in improved agreement between theoretical and observed hydrocarbon and cyanoacetylene abundances. The reaction between  $C_3H^+$  and  $H_2$  does proceed to form  $C_3H_2^+ + H$  at 80 K if the reactant ion is translationally hot. The importance of this process in the interstellar medium is discussed.

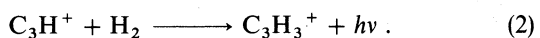
*Subject headings:* interstellar: molecules — molecular processes — nebulae: individual

## I. INTRODUCTION

In 1983, Herbst, Adams, and Smith published the rate coefficients of a variety of ion-molecule reactions of possible importance for the gas phase chemistry of dense interstellar clouds. The studied reactions were of two types: hydrogenation reactions between hydrocarbon ions and  $H_2$ , and reactions between  $C^+$  and hydrocarbon neutrals. It was found that most important hydrogenation reactions between  $H_2$  and multi-carbon hydrocarbon ions (viz.,  $C_2H_3^+$ ,  $C_2H_4^+$ ,  $C_2H_5^+$ ,  $C_3H_2^+$ ,  $C_3H_3^+$ ,  $C_3H_4^+$ ,  $C_3H_5^+$ ,  $C_3H_7^+$ ,  $C_4H^+$ ) do not proceed rapidly in the laboratory via either a normal two-body channel or even via three-body association. Several recent models of the gas phase chemistry of dense interstellar clouds (Herbst 1983; Millar and Freeman 1984a, b; Leung, Herbst, and Huebner 1984) have utilized some of these results. However, it has been brought to our attention (Bohme 1983) and confirmed by us that we erroneously reported one of our results. Specifically, the reaction between  $C_3H^+$  and  $H_2$  for reactant species at 80 K was reported to produce  $C_3H_2^+ + H$  with a two-body rate coefficient of  $1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . In reality, the product at 80 K is not  $C_3H_2^+$  but only  $C_3H_3^+$  which is formed via a saturated three-body association mechanism of the type



where the lifetime of the  $C_3H_3^{+*}$  "complex" is sufficiently long that, once formed, it has zero chance of redissociation into reactants at the pressure of our experiments. Thus, there is no dependence of the reaction rate on helium pressure, and an effective two-body reaction results with a rate coefficient of  $1.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , implying a very large three-body rate coefficient. Under interstellar conditions, the saturated three-body association mechanism is replaced by a radiative association mechanism of the type



The saturated rate coefficient measured for process (1) is not particularly useful for indirectly obtaining the rate coefficient of process (2) but can yield a lower limit to this rate. However, at a temperature of 550 K, process (1) is no longer saturated at all studied pressures, and a three-body rate coefficient of  $4 \times 10^{-28} \text{ cm}^6 \text{ s}^{-1}$  can be obtained from the data. Using the expected temperature dependence of the association reaction rate coefficient ( $T^{-1.5} - T^{-2.5}$ ; Smith *et al.* 1983) and the usual complex radiative stabilization rate of  $10^2 \text{ s}^{-1}$ , we obtain a rate for reaction (2) of  $\sim 4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at 10 K with at least an order of magnitude uncertainty. Using the purely theoretical "modified thermal" approach (Bates 1979; Herbst 1980), we obtain a rate coefficient of  $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , also with an order of magnitude uncertainty. In the model calculations discussed below, a value of  $\sim 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  is assumed for  $k_2$ .

Via use of a new drift tube described elsewhere (Smith, Adams, and Alge 1984; Adams and Smith 1984), we have found that the bimolecular reaction

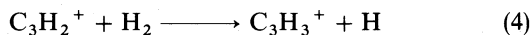


can also occur at 80 K if the reactant ion is supplied with a small amount of additional translational (kinetic) energy. For example, at 80 K an additional relative kinetic energy of only 27 meV (1 meV = 11.6 K) between ion and neutral is sufficient to permit reaction (3) to proceed with a rate coefficient of  $6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . Reaction (1) also occurs but at a reduced rate of  $3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . At temperatures of 295 K and 550 K, there is enough thermal energy to power reaction (3) in direct competition with reaction (1). It is unclear whether the competition in the laboratory between reactions (1) and (3) is due to reaction along two completely separate pathways, one of which possesses a small amount of activation energy, or whether reaction (3) occurs as a result of  $C_3H_3^{+*}$  complex formation followed by dissociation of complexes with sufficient energy to form  $C_3H_2^+ + H$ . More laboratory and theoretical work is planned to elucidate the situation.

In dense interstellar clouds, C<sub>3</sub>H<sup>+</sup> is produced via ion-molecule reactions with some initial nonthermal translational energy. For example, the important reaction between C<sub>3</sub><sup>+</sup> and H<sub>2</sub>, which produces C<sub>3</sub>H<sup>+</sup> and H, is exothermic by ~1.5 eV. If we assume that ~1 eV of this energy goes into product translation, the C<sub>3</sub>H<sup>+</sup> ion will obtain only 1/37 of this, or 40 meV, due to its large mass compared with atomic hydrogen. As the C<sub>3</sub>H<sup>+</sup> cools via elastic collisions with H<sub>2</sub>, there is a finite chance of reaction (2) or (3) occurring instead. Since H<sub>2</sub> is very light compared with C<sub>3</sub>H<sup>+</sup>, it may be inefficient at translational relaxation, and it seems prudent to suggest that as many as 10 collisions would be required to thermalize C<sub>3</sub>H<sup>+</sup>. If we assign a typical rate coefficient of ~10<sup>-9</sup> cm<sup>3</sup> s<sup>-1</sup> for collisions, then an effective rate coefficient for cooling would be ~10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup>. This is only 10 times the size of the rate coefficient for reaction (3) measured for a relative translational energy of 27 meV. We can crudely estimate therefore that ~90% of the C<sub>3</sub>H<sup>+</sup> ions relax and ~10% react with H<sub>2</sub> to form C<sub>3</sub>H<sub>2</sub><sup>+</sup>. We have ignored the possibility of radiative association (reaction [2]) of excited C<sub>3</sub>H<sup>+</sup> ions because radiative association rate coefficients decrease with increasing translational energy. The 90% figure discussed above may well be a severe lower limit for C<sub>3</sub>H<sup>+</sup> since much of the energy available in exothermic ion-molecule reactions is known to go into product internal energy modes where, in interstellar clouds, it would be radiated away.

To attempt a more serious estimate of the amount of C<sub>3</sub>H<sub>2</sub><sup>+</sup> produced via reaction (3) in dense clouds, we would have to know the initial translational energy distribution of C<sub>3</sub>H<sup>+</sup> (formed via several different exothermic reactions), the rate of C<sub>3</sub>H<sup>+</sup> cooling via H<sub>2</sub> collisions, and the rate of reaction (3) as a function of kinetic energy. Since we do not know these quantities, and since there are competing pathways for C<sub>3</sub>H<sub>2</sub><sup>+</sup> production in models such as that of Herbst (1983), we ignore this nonthermal route to C<sub>3</sub>H<sub>2</sub><sup>+</sup> production. Our only important assumption is that it does not seriously impede the radiative association route to C<sub>3</sub>H<sub>3</sub><sup>+</sup>, which is important for complex molecule synthesis. This assumption seems reasonable because the other reactions that produce C<sub>3</sub>H<sup>+</sup> tend to produce light species (H or H<sub>2</sub>) as the other product. Therefore little kinetic energy goes into C<sub>3</sub>H<sup>+</sup> initially.

The question of the importance of other nonthermal reactions between translationally hot ions and H<sub>2</sub> remains an interesting one which merits further study. It is possible that some other hydrogenation reactions measured by Herbst, Adams, and Smith (1983) not to occur under thermal conditions can occur for translationally hot ions. For example, preliminary measurements show that the reaction



is also switched on in this manner. At 80 K, a relative translational energy of 70 meV results in a rate coefficient of 3 × 10<sup>-12</sup> cm<sup>3</sup> s<sup>-1</sup>. Once again, the importance of this reaction in interstellar clouds cannot be easily ascertained from the data at hand. Note, however, that even if reaction (3) siphoned off a significant amount of C<sub>3</sub>H<sup>+</sup> to produce C<sub>3</sub>H<sub>2</sub><sup>+</sup> rather than C<sub>3</sub>H<sub>3</sub><sup>+</sup>, reaction (4) could serve to regenerate the C<sub>3</sub>H<sub>3</sub><sup>+</sup>.

To determine the importance of our original error in reporting the products of the reaction of C<sub>3</sub>H<sup>+</sup> and H<sub>2</sub> under thermal conditions to be C<sub>3</sub>H<sub>2</sub><sup>+</sup> + H instead of C<sub>3</sub>H<sub>3</sub><sup>+</sup>, we have redone the "semidetailed" steady-state TMC-1 model of Herbst (1983). In performing this calculation, we have also

changed the rate coefficient for the important radiative association reaction



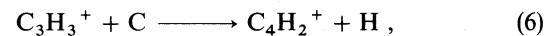
from the previously used theoretical value of 1.0 × 10<sup>-14</sup> cm<sup>3</sup> s<sup>-1</sup> to a newly measured experimental value at 13 K of 1.8 × 10<sup>-13</sup> cm<sup>3</sup> s<sup>-1</sup> (Barlow, Dunn, and Schauer 1984). This value is in order-of-magnitude agreement with estimates based on the three-body data of Adams and Smith (1981) at 82 K. The effect of both changes is to enhance somewhat the calculated abundances of complex species such as C<sub>3</sub>H<sub>4</sub>, C<sub>4</sub>H, and HC<sub>3</sub>N.

## II. MODEL CALCULATION

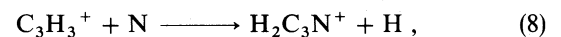
The "semidetailed" dense cloud model of Herbst (1983) is one in which the abundances of selected atomic and small molecular species are fixed at observed or estimated values and the abundances of selected hydrocarbons and cyanoacetylenes calculated in the steady-state limit. Herbst (1983) found that in order to reproduce the observed abundances of species such as CH, C<sub>2</sub>H, C<sub>3</sub>H<sub>4</sub> (methyl acetylene), C<sub>4</sub>H, and C<sub>3</sub>N in TMC-1, he was forced to assume a high fractional abundance for C I of 10<sup>-5</sup>. His results are in agreement with those of the more detailed, time-dependent model of Leung, Herbst, and Huebner (1984) in which significant complex molecule abundances are achieved mainly at young cloud lifetimes when a relatively large abundance of C I is present.

The results of our new calculations using Herbst's model are shown in Table 1, where they are compared with his previous calculated abundances and observed abundances in TMC-1. Table 1 contains the results of four sets of calculations—labeled 1, 2, 3, and 4. Calculations 2, 3, and 4 are new whereas calculation 1 refers to Herbst's previous work, specifically his cloud 5, in which a high C I abundance was assumed. Our calculations 2 and 3 were undertaken with the same set of fixed abundances as calculation 1 (see Table 1). For calculation 2 the C<sub>3</sub>H<sup>+</sup> + H<sub>2</sub> reaction was changed to a radiative association one with k<sub>2</sub> = 1 × 10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup>, whereas for calculation 3 the new experimental value for k<sub>5</sub> was used as well. Both of these changes were also incorporated into calculation 4, in which the C I fractional abundance was reduced to 3 × 10<sup>-6</sup> to determine whether or not a C I abundance of ~10<sup>-5</sup> is critical. All calculations have reaction rates based on a temperature of 10 K, which pertains to TMC-1.

As part of a discussion of our results, it is useful to explain how changes in the reactions discussed above can affect the calculated abundances of species such as C<sub>3</sub>H<sub>4</sub> (methyl acetylene), C<sub>4</sub>H, and HC<sub>3</sub>N. The inclusion of a radiative association reaction between C<sub>3</sub>H<sup>+</sup> and H<sub>2</sub> opens up a new and important channel for C<sub>3</sub>H<sub>3</sub><sup>+</sup> production. This ion is a precursor of both C<sub>4</sub>H and HC<sub>3</sub>N which are produced in the model via the reaction sequences



and



It is not surprising, therefore, that comparison of calculation 2 with calculation 1 shows an increase in the calculated abun-

TABLE 1  
 RESULTS FOR TMC-1<sup>a</sup>

FRACTIONAL ABUNDANCE <sup>b</sup>	CALCULATED RESULTS				OBSERVATIONAL RESULTS
	1	2	3	4	
Fixed					
$f_C$ .....	1.0(-5)	1.0(-5)	1.0(-5)	3.0(-6)	...
$f_O$ .....	5.0(-5)	5.0(-5)	5.0(-5)	5.0(-5)	$\leq 2(-4)^c$
$f_N$ .....	1.0(-5)	1.0(-5)	1.0(-5)	1.0(-5)	...
$f_{CO}$ .....	6.0(-5)	6.0(-5)	6.0(-5)	6.0(-5)	$6(-5)^d$
$f_{C^+}$ .....	1.0(-9)	1.0(-9)	1.0(-9)	1.0(-9)	...
$f_{H^+}$ .....	1.0(-9)	1.0(-9)	1.0(-9)	1.0(-9)	...
$f_{He^+}$ .....	1.0(-9)	1.0(-9)	1.0(-9)	1.0(-9)	...
$f_{HCO^+}$ .....	8.0(-9)	8.0(-9)	8.0(-9)	8.0(-9)	$8(-9)^e$
$f_{H_3^+}$ .....	3.0(-9)	3.0(-9)	3.0(-9)	3.0(-9)	...
$f_e$ .....	3.0(-8)	3.0(-8)	3.0(-8)	3.0(-8)	$8(-9)-1(-7)^c$
Calculated					
$f_{CH}$ .....	5.7(-8)	5.8(-8)	4.8(-8)	1.5(-8)	$2(-8)^g$
$f_{CH_2}$ .....	5.7(-8)	5.7(-8)	5.1(-8)	2.6(-8)	...
$f_{CH_3}$ .....	1.3(-9)	1.3(-9)	8.9(-9)	4.1(-9)	...
$f_{CH_4}$ .....	4.9(-7)	4.9(-7)	3.9(-6)	1.9(-6)	...
$f_{C_2}$ .....	2.8(-8)	2.8(-8)	3.5(-8)	4.2(-9)	$5(-8)^f$
$f_{C_2H}$ .....	2.2(-8)	2.3(-8)	3.2(-8)	7.1(-9)	$8(-9)^g$
$f_{C_2H_2}$ .....	1.2(-7)	1.6(-7)	4.2(-7)	1.1(-7)	...
$f_{C_2H_3}$ .....	8.1(-8)	8.2(-8)	1.6(-7)	3.9(-8)	...
$f_{C_2H_4}$ .....	5.7(-9)	5.7(-9)	2.3(-8)	4.8(-9)	...
$f_{C_3}$ .....	8.7(-9)	7.5(-9)	1.6(-8)	1.7(-9)	...
$f_{C_3H}$ .....	1.2(-7)	1.4(-7)	2.5(-7)	4.3(-8)	...
$f_{C_3H_2}$ .....	1.7(-8)	9.1(-8)	1.5(-7)	2.5(-8)	...
$f_{C_3H_3}$ .....	2.4(-9)	2.5(-9)	1.4(-8)	2.2(-9)	...
$f_{C_3H_4}$ .....	8.2(-10)	8.4(-10)	7.7(-9)	1.3(-9)	$6(-9)^h$
$f_{C_4}$ .....	3.3(-9)	4.7(-9)	9.9(-9)	6.6(-10)	...
$f_{C_4H}$ .....	1.3(-8)	3.7(-8)	1.2(-7)	7.6(-9)	$2(-8)^{h,i}$
$f_{C_4H_2}$ .....	3.7(-9)	4.3(-9)	4.2(-8)	3.2(-9)	...
$f_{C_2N}$ .....	2.3(-9)	2.7(-9)	5.1(-9)	1.2(-9)	...
$f_{C_3N}$ .....	1.2(-9)	1.6(-9)	2.9(-9)	4.9(-10)	$1(-9)^j$
$f_{HC_3N}$ .....	2.6(-10)	1.3(-9)	2.2(-9)	3.6(-10)	$6(-9)^j$
$f_{CH_3^+}$ .....	6.3(-10)	6.3(-10)	2.7(-10)	1.0(-10)	...
$f_{CH_5^+}$ .....	7.5(-11)	7.5(-11)	6.0(-10)	2.7(-10)	...
$f_{C_2H_2^+}$ .....	1.2(-10)	1.2(-10)	9.3(-11)	2.4(-11)	...
$f_{C_2H_3^+}$ .....	4.8(-11)	5.6(-11)	2.3(-10)	7.5(-11)	...
$f_{C_3H_2^+}$ .....	1.1(-10)	5.7(-11)	1.1(-10)	2.0(-11)	...
$f_{C_3H_3^+}$ .....	1.6(-11)	9.1(-11)	1.5(-10)	2.5(-11)	...

<sup>a</sup> Notation  $a(-b)$  signifies  $a \times 10^{-b}$ .

<sup>b</sup> With respect to  $H_2$ .

<sup>c</sup> Guélin, Langer, and Wilson 1982 and references therein.

<sup>d</sup> Allen and Knapp 1978.

<sup>e</sup> Brown 1981.

<sup>f</sup> Hobbs, Black, and Van Dishoeck 1983.

<sup>g</sup> Wootten *et al.* 1980.

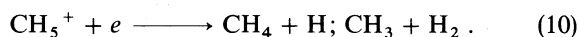
<sup>h</sup> Irvine *et al.* 1981.

<sup>i</sup> Guélin, Friberg, and Mezaoui 1982.

<sup>j</sup> Large collection of references in Hjalmarsen and Irvine 1983.

dances of  $C_3H_3^+$ ,  $C_4H$ , and  $HC_3N$  when the  $C_3H^+ + H_2$  association reaction is utilized. Note that these numerical results are independent of the specific rate coefficient used for  $C_3H^+ + H_2$  as long as this process is the rate-determining destruction step for  $C_3H^+$  ( $k_2 > 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  under the cloud conditions chosen).

The increase in the rate coefficient of the  $CH_3^+ + H_2$  radiative association reaction has the effect of reducing the  $CH_3^+$  abundance and increasing the  $CH_3$  and  $CH_4$  abundances via



These increases lead to increases in the abundances of more complex hydrocarbon species via "condensation" reactions between  $CH_3$ ,  $CH_4$  and hydrocarbon ions, as well as reactions

between  $C^+$  and  $CH_4$  and/or  $CH_3$ . The reader is advised to view the synthetic ion-molecule reaction sequences in Herbst (1983) to observe the various ways in which an increase in  $CH_3$  and  $CH_4$  production can propagate into increases into the abundances of more complex hydrocarbon species. Abundances of cyanoacetylenes also increase due to increased abundances of precursor ions such as  $C_3H_3^+$ . The calculated increases in abundances are clearly seen by comparing the results of calculations 3 with calculations 1 and 2.

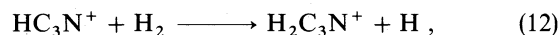
If we compare the abundances of calculation 3 with observed abundances in TMC-1, we find excellent agreement for all species in the calculation with observed abundances. As compared with Herbst's earlier work (calculation 1), the disagreements between theory and observation for  $C_3H_4$  and  $HC_3N$

have been removed. The newly calculated abundances of CH, C<sub>2</sub>, C<sub>2</sub>H, and C<sub>3</sub>N are still in reasonable agreement with observation. The new value for the C<sub>4</sub>H abundance is a factor of 6 higher than what is observed. Agreement can be improved by assuming a rapid rate for the reaction C<sub>4</sub>H + O, in analogy with Herbst's earlier assumption of a rapid rate for the reaction between C<sub>2</sub>H and O.

In calculation 4, the fractional abundance of C I has been reduced to  $3 \times 10^{-6}$ . Calculated abundances of C<sub>2</sub>, C<sub>3</sub>H<sub>4</sub>, and especially HC<sub>3</sub>N are somewhat low compared with observed values. Still, only the calculated abundance of HC<sub>3</sub>N is low by over an order of magnitude.

Despite the success of the model, we remind the reader that in ion-molecule models of complex molecule formation, important reactions have yet to be studied in the laboratory. Reactions (6) and (8) belong to this category. In addition, the conservation of electronic spin angular momentum in reaction (8) suggests that only an excited triplet electronic state of H<sub>2</sub>C<sub>3</sub>N<sup>+</sup> can be formed efficiently. If this state is sufficiently high in energy, the reaction will be effectively endothermic. Another path to HC<sub>3</sub>N production which avoids this possi-

bility is the route (Millar and Freeman 1984*a, b*; Leung, Herbst, and Huebner 1983)



followed by reaction (9). This pathway was not included by Herbst (1983) because reaction (12) has not been studied in the laboratory and hydrogenation reactions often possess activation energy barriers. Reaction (12) will be studied in the laboratory in a short period of time (McEwan 1983). Its inclusion in other models at a rate of  $\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  (Millar and Freeman 1984*a, b*; Leung, Herbst, and Huebner 1984) also results in a reproduction of the observed HC<sub>3</sub>N abundance in TMC-1.

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