

– Supplementary material –

**Knowledge-based probabilistic representations  
of branching ratios in chemical networks:  
the case of dissociative recombinations**

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## I. THE DATABASE

Models of ion-neutral chemistry generally include DR processes through the reaction rate constant

$$\alpha(T_e) = \alpha_0 \times (T_e/T_0)^{-\beta} \quad (1)$$

where  $\alpha_0$  is the rate constant at a reference electron temperature  $T_0$  (typically 300 K), and  $T_e$  is the electron temperature of interest. When more than one product channel is accessible, the partial rate for channel  $i$  is  $\alpha_i(T_e) = b_i \times \alpha(T_e)$ , where  $\{b_i, i = 1, N\}$  are the *branching ratios* of the reaction. As the global DR rate  $\alpha(T_e)$  and the branching ratios  $\{b_i\}$  are typically derived from different experiments, they are treated separately.

The following tables report data for ions identified in Titan’s ionosphere. **At the present stage, this is a demonstration database for the use of Nested Dirichlet representations of uncertain branching ratios, and it should not be considered or used as a reference database without caution.**

### A. Rate parameters

The present article being focussed on branching ratios and their uncertainties, the DR rate coefficients were taken at their nominal value.

Reaction	$\alpha_0(cm^3.s^{-1})$	$\beta$
$H_2^+ + e^-$	$1.6 \times 10^{-6}$ [1]	0.43 [1]
$H_3^+ + e^-$	$7.2 \times 10^{-8}$ [2–4]	0.74 [1, 5–7]
$C^+ + e^-$	$4.67 \times 10^{-12}$ [8, 9]	0.6 [9]
$CH^+ + e^-$	$1.73 \times 10^{-7}$ [1, 9–11]	0.63 [1, 9–11]
$CH_2^+ + e^-$	$4.66 \times 10^{-7}$ [10, 12]	0.55 [10, 12]
$CH_3^+ + e^-$	$6.54 \times 10^{-7}$ [1, 10, 11]	0.51 [1, 10, 11]
$CH_4^+ + e^-$	$6.69 \times 10^{-7}$ [1, 10, 11]	0.51 [1, 10, 11]
$CH_5^+ + e^-$	$6.26 \times 10^{-7}$ [1, 10, 11, 13–17]	0.65 ( $T_e \leq 300$ K); 1.5 ( $T_e \geq 300$ K) [1, 10, 11, 13, 16, 17]
$C_2H^+ + e^-$	$2.7 \times 10^{-7}$ [1, 18]	0.76 [1, 11, 18]
$C_2H_2^+ + e^-$	$5.20 \times 10^{-7}$ [1, 11]	0.75 [1, 11]
$C_2H_3^+ + e^-$	$8.49 \times 10^{-7}$ [1, 11, 19, 20]	0.84 ( $T_e \leq 800$ K) [1, 11, 19, 20]; 1.44 ( $T_e \geq 800$ K) [19, 20]

<b>Reaction</b>	$\alpha_0(cm^3.s^{-1})$	$\beta$
$C_2H_4^+ + e^-$	$5.6 \times 10^{-7}$ [18]	0.76 [18, 20]
$C_2H_5^+ + e^-$	$8.35 \times 10^{-7}$ [1, 14, 15, 17]	0.8 ( $T_e \leq 300$ K) [17]; 1.2 ( $T_e \geq 300$ K) [17]
$C_3^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$C_3H^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$C_3H_2^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$c - C_3H_3^+ + e^-$	$8.00 \times 10^{-7}$ [21]	0.0 [1, 11, 20]
$l - C_3H_3^+ + e^-$	$1.15 \times 10^{-7}$ [1, 11, 20]	0.0 [1, 11, 20]
$C_3H_4^+ + e^-$	$2.95 \times 10^{-6}$ [22]	0.67 [22]
$C_3H_5^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$C_3H_6^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$C_3H_7^+ + e^-$	$1.22 \times 10^{-6}$ [14, 23, 24]	0.68 [23]
$C_3H_8^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$C_4H^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$C_4H_2^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$C_4H_3^+ + e^-$	$6.2 \times 10^{-7}$ [1, 11, 25]	1.00 [Note 6]
$C_4H_4^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$C_4H_5^+ + e^-$	$8.2 \times 10^{-7}$ [26]	1.00 [Note 6]
$C_4H_6^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$C_4H_7^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$C_4H_8^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$C_4H_9^+ + e^-$	$8.3 \times 10^{-7}$ [14]	1.00 [Note 6]
$N^+ + e^-$	$4.0 \times 10^{-12}$ [8, 9]	0.58 [8, 9]
$NH^+ + e^-$	$4.33 \times 10^{-8}$ [1, 9, 11]	1.00 [Note 6]
$NH_2^+ + e^-$	$2.24 \times 10^{-7}$ [Note 3(a)]	1.00 [Note 6]
$NH_3^+ + e^-$	$3.1 \times 10^{-7}$ [9]	1.00 [Note 6]
$NH_4^+ + e^-$	$1.16 \times 10^{-6}$ [1, 11, 27–29]	0.75 [1, 11, 28, 29]
$N_2^+ + e^-$	$2.2 \times 10^{-7}$ [30–37]	0.35 [30, 31, 33, 34, 37]
$N_2H^+ + e^-$	$2 \times 10^{-7}$ [1, 11, 13, 38–43]	0.5 [38, 41–43]
$CN^+ + e^-$	$3.4 \times 10^{-7}$ [44]	0.55 [20, 44]
$HCN^+ + e^-$	$2.5 \times 10^{-6}$ [45]	1.00 [45]
$HNC^+ + e^-$	$1.3 \times 10^{-7}$ [45, 46]	0.98 [45, 46]

<b>Reaction</b>	$\alpha_0(cm^3.s^{-1})$	$\beta$
$HCNH^+ + e^-$	$3.2 \times 10^{-7}$ [1, 47–49]	1.01 [47, 49]
$CH_2NH_2^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$CH_3CNH^+ + e^-$	$3.3 \times 10^{-7}$ [1, 11, 35, 48, 49]	1.03 [49]
$C_2N_2^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$C_3N^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$CHCCN^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$CHCCNH^+ + e^-$	$1.22 \times 10^{-6}$ [Note 3(b)]	1.00 [Note 6]
$CH_2CHCNH^+ + e^-$	$1.76 \times 10^{-6}$ [50]	0.80 [50]
$OH^+ + e^-$	$3.75 \times 10^{-8}$ [1, 9, 11, 51]	0.5 [1, 9, 11, 51]
$H_2O^+ + e^-$	$3.34 \times 10^{-7}$ [1, 11, 52, 53]	0.77 [1, 11]
$H_3O^+ + e^-$	$8 \times 10^{-7}$ [1, 15, 54, 55]	0.9 [54, 56]
$CO^+ + e^-$	$2.0 \times 10^{-7}$ [35, 57, 58]	0.55 [57]
$HCO^+ + e^-$	$2.1 \times 10^{-7}$ [1, 9, 11, 13, 38, 42, 59–62]	0.69 [1, 9, 11, 20, 38, 42]
$CH_2OH^+ + e^-$	$7 \times 10^{-7}$ [63]	0.78 [63]
$NO^+ + e^-$	$4 \times 10^{-7}$ [1, 9, 32, 64–66]	0.8 [1, 9, 66]

1. *Notes for rate constant parameters*

The guidelines we followed to establish the nominal values for both rate parameters  $\alpha_0$  and  $\beta$  in Eq. 1 are described here.

1.  $\alpha_0$ : when a single reference value was available, it was taken at face value;
2.  $\alpha_0$ : when several reference values were found:
  - (a) with discrepant values: the most recent was considered;
  - (b) with compatible values: the mean value of a loguniform distribution covering all values was used. This was retained to compensate for the absence of uncertainty statement in some references.
3.  $\alpha_0$ : when no reference values were available, we used the mean values of loguniform distributions covering intervals with limits defined by existing rates for similar ions:

- (a) for light species (less than 3 heavy atoms) the interval is  $[5 \times 10^{-8}, 1 \times 10^{-6}] \text{ cm}^3.\text{s}^{-1}$ , and the nominal value is  $2.24 \times 10^{-7} \text{ cm}^3.\text{s}^{-1}$ ; *e.g.*  $\text{NH}_2^+$ ;
  - (b) for heavy species, presenting generally enhanced reaction rates, the interval is  $[5 \times 10^{-7}, 3 \times 10^{-6}] \text{ cm}^3.\text{s}^{-1}$ , and the nominal value is  $1.22 \times 10^{-6} \text{ cm}^3.\text{s}^{-1}$ ; *e.g.*  $\text{C}_3\text{H}_5^+$ ,  $\text{C}_4\text{H}_7^+$ ...
4.  $\beta$ : when a single reference value was available, it was taken at face value;
  5.  $\beta$ : when several reference values were found, we used the mean of a uniform interval covering these values, *i.e.*  $\beta = (\beta_{min} + \beta_{max})/2$ ;
  6.  $\beta$ : when no reference values were available, the mean value of the largest interval as defined by the theoretical values of  $\beta$  for direct and indirect processes was used, *i.e.*  $\beta = (0.5 + 1.5)/2 = 1$ .

## B. Branching ratios

Information on branching ratios is typically sparser than for reaction rates, and it is exceptional to have to consider conflicting data. The following set of considerations is used in order to define the structures of the (Nested) Dirichlet distributions.

*a. Maximum number of fragments.* In absence of experimentally characterized products, one should consider all the exoergic channels and state a total lack of knowledge on the corresponding branching ratios (Diun distribution). It is not possible to make further hypotheses wrt. the relative stability of the products. From Ref. [1], we know for instance that the measured branching ratios have no definite correlation with the exoergicity of the pathways. An issue in building a list of exoergic pathways is the number of fragments that can be accepted in each pathway. For instance, on the basis of their previous results, for  $\text{C}_3\text{H}_7^+$  Ehlerding *et al.*[23] stop at a three body breakup pattern, even though some four body channels are opened ( $\text{C}_3\text{H}_3 + \text{H}_2 + 2\text{H}$ ,  $\text{C}_2\text{H}_2 + \text{CH}_3 + 2\text{H}$ ). Other authors consider also four body breakup patterns in their analysis:  $\text{CD}_3\text{CDO}^+$ , [67]  $\text{CD}_3\text{CND}^+$ , [68] and  $\text{CH}_2\text{CHCNH}^+$ . [50] In the present treatment, we favored an exhaustive treatment and we enabled four body breakups when possible.

*b.  $\text{H}_2$  vs.  $2\text{H}$ .* An empirical rule appears throughout the database of branching ratios: the loss of 2 H atoms is more – often much more – probable than the loss of an  $\text{H}_2$  molecule. The only measured exception is  $\text{NH}_4^+$ . This rule is used to reduce uncertainty by nesting both pathways using a Dior distribution.

*c. Heavy fragments as a basis for nesting.* A corrolary of the previous rule is that we are often induced to nest together pathways involving the same heavy fragment (e.g.  $\text{X} + 2\text{H}$  and  $\text{X} + \text{H}_2$ ). For hydrocarbons, and in absence of experimental values, we adopted this as a general guideline to ensure a balanced treatment amongst those heavy fragments. This rule becomes ambiguous for N-bearing molecules and was restricted to hydrocarbon ions.

*d. Spin states.* Some species in the photochemical model have specified spin states. This is mostly the case for  $\text{CH}_2$  and N. When the spin states of DR products have not been measured, we nest them inside a uniform Dirichlet subtree.

Reaction	Products	Branching ratios
$\text{H}_2^+ + \text{e}^-$	$\rightarrow 2 \text{H}$	-
$\text{H}_3^+ + \text{e}^-$	$\rightarrow \text{H}_3$	$0.00 - 0.09$ [1]
	$\rightarrow \text{H}_2 + \text{H}$	$0.25 - 0.40$ [1, 6]
	$\rightarrow 3 \text{H}$	$0.51 - 0.75$ [1, 6]
$\text{C}^+ + \text{e}^-$	$\rightarrow \text{C} + \text{h}\nu$	-
$\text{CH}^+ + \text{e}^-$	$\rightarrow \text{C} + \text{H}$	-
$\text{CH}_2^+ + \text{e}^-$	$\rightarrow \text{CH} + \text{H}$	$0.25 \pm 0.04$ [12]
	$\rightarrow \text{C} + \text{H}_2$	$0.12 \pm 0.02$
	$\rightarrow \text{C} + 2 \text{H}$	$0.63 \pm 0.06$
$\text{CH}_3^+ + \text{e}^-$	$\rightarrow \begin{cases} {}^1\text{CH}_2 + \text{H} \\ {}^3\text{CH}_2 + \text{H} \end{cases}$	$0.40 \pm 0.1$ [69]
	$\rightarrow \text{CH} + \text{H}_2$	$0.14 \pm 0.1$
	$\rightarrow \text{CH} + 2 \text{H}$	$0.16 \pm 0.15$
	$\rightarrow \text{C} + \text{H}_2 + \text{H}$	$0.30 \pm 0.08$
$\text{CH}_4^+ + \text{e}^-$	$\rightarrow \begin{cases} \text{CH}_3 + \text{H} \\ \begin{cases} {}^1\text{CH}_2 + \text{H}_2 \\ {}^3\text{CH}_2 + \text{H}_2 \end{cases} \\ \begin{cases} {}^1\text{CH}_2 + 2 \text{H} \\ {}^3\text{CH}_2 + 2 \text{H} \end{cases} \\ \text{CH} + \text{H}_2 + \text{H} \\ \text{CH} + 3 \text{H} \\ \text{C} + 2 \text{H}_2 \end{cases}$	Exoergic channels
$\text{CH}_5^+ + \text{e}^-$	$\rightarrow \text{CH}_4 + \text{H}$	$0.049 \pm 0.013$ [16]; $0.95 \pm 0.05$ [70] [Note 4]
	$\rightarrow \text{CH}_3 + \text{H}_2$ (a)	$0.048 \pm 0.002$ [16]; (a) + (b) $\leq 0.08$ [70]
	$\rightarrow \text{CH}_3 + 2 \text{H}$ (b)	$0.698 \pm 0.008$ [16]; (a) + (b) $\leq 0.08$ [70]
	$\rightarrow \begin{cases} {}^1\text{CH}_2 + \text{H}_2 + \text{H} \\ {}^3\text{CH}_2 + \text{H}_2 + \text{H} \end{cases}$	$0.172 \pm 0.016$ [16]; $\leq 0.01$ [70]
	$\rightarrow \text{CH} + 2 \text{H}_2$	$0.033 \pm 0.011$ [16]; $\leq 0.01$ [70]
$\text{C}_2\text{H}^+ + \text{e}^-$	$\rightarrow \text{C}_2 + \text{H}$	$0.43 \pm 0.03$ [18]
	$\rightarrow \text{CH} + \text{C}$	$0.39 \pm 0.04$
	$\rightarrow 2 \text{C} + \text{H}$	$0.18 \pm 0.04$
$\text{C}_2\text{H}_2^+ + \text{e}^-$	$\rightarrow \text{C}_2\text{H} + \text{H}$	$0.50 \pm 0.06$ [71]

Reaction	Products	Branching ratios
	$\rightarrow \text{C}_2 + 2\text{H}$	$0.30 \pm 0.05$
	$\rightarrow \text{C}_2 + \text{H}_2$	$0.02 \pm 0.03$
	$\rightarrow \begin{cases} {}^1\text{CH}_2 + \text{C} \\ {}^3\text{CH}_2 + \text{C} \end{cases}$	$0.05 \pm 0.01$
	$\rightarrow 2\text{CH}$	$0.13 \pm 0.01$
$\text{C}_2\text{H}_3^+ + \text{e}^-$	$\rightarrow \text{C}_2\text{H}_2 + \text{H}$	$0.29 \pm 0.04$ [19]
	$\rightarrow \text{C}_2\text{H} + \text{H}_2$	$0.06 \pm 0.03$
	$\rightarrow \text{C}_2\text{H} + 2\text{H}$	$0.584 \pm 0.06$ for $\sum = 1$ (0.59)
	$\rightarrow \text{C}_2 + \text{H} + \text{H}_2$	$0.03 \pm 0.01$
	$\rightarrow \text{CH}_3 + \text{C}$	$0.006 \pm 0.002$
	$\rightarrow \begin{cases} {}^1\text{CH}_2 + \text{CH} \\ {}^3\text{CH}_2 + \text{CH} \end{cases}$	$0.03 \pm 0.01$
$\text{C}_2\text{H}_4^+ + \text{e}^-$	$\rightarrow \text{C}_2\text{H}_3 + \text{H}$	$0.11 \pm 0.07$ [18]
	$\rightarrow \text{C}_2\text{H}_2 + \text{H}_2$	$0.06 \pm 0.03$
	$\rightarrow \text{C}_2\text{H}_2 + 2\text{H}$	$0.66 \pm 0.06$
	$\rightarrow \text{C}_2\text{H} + \text{H}_2 + \text{H}$	$0.10 \pm 0.04$
	$\rightarrow \text{CH}_4 + \text{C}$	$0.01 \pm 0.01$
	$\rightarrow \text{CH}_3 + \text{CH}$	$0.02 \pm 0.02$
	$\rightarrow \begin{cases} {}^1\text{CH}_2 + {}^1\text{CH}_2 \\ {}^1\text{CH}_2 + {}^3\text{CH}_2 \\ {}^3\text{CH}_2 + {}^3\text{CH}_2 \end{cases}$	$0.04 \pm 0.02$
$\text{C}_2\text{H}_5^+ + \text{e}^-$	$\rightarrow \text{C}_2\text{H}_4 + \text{H}$	$0.12 \pm 0.03$ [72] [Note 5]
	$\rightarrow \text{C}_2\text{H}_3 + 2\text{H}$	$0.27 \pm 0.04$
	$\rightarrow \text{C}_2\text{H}_2 + 3\text{H}$	$0.13 \pm 0.03$
	$\rightarrow \text{C}_2\text{H}_2 + \text{H}_2 + \text{H}$	$0.30 \pm 0.03$ for $\sum = 1$ (0.29)
	$\rightarrow \begin{cases} \text{CH}_3 + {}^1\text{CH}_2 \\ \text{CH}_3 + {}^3\text{CH}_2 \end{cases}$	$0.17 \pm 0.01$
	$\rightarrow \text{CH}_4 + \text{CH}$	$0.01 \pm 0.01$
$\text{C}_3^+ + \text{e}^-$	$\rightarrow \text{C}_3$	$0.000 \pm 0.001$ [20, 73]
	$\rightarrow \text{C}_2 + \text{C}$	$1.000 \pm 0.002$
	$\rightarrow 3\text{C}$	$0.000 \pm 0.001$
$\text{C}_3\text{H}^+ + \text{e}^-$	$\rightarrow \text{C}_3 + \text{H}$	$0.662 \pm 0.015$ [1, 11, 74, 75]



Reaction	Products	Branching ratios
	$\rightarrow \text{C}_2\text{H} + \text{C}$	$0.338 \pm 0.017$
	$\rightarrow \text{C}_2 + \text{CH}$	$0.00 \pm 0.01$
$\text{C}_3\text{H}_2^+ + \text{e}^-$	$\rightarrow \left\{ \begin{array}{l} \text{C}_3 + \text{H}_2 \\ \text{C}_3 + 2\text{H} \\ \text{C}_3\text{H} + \text{H} \\ \text{C}_2\text{H}_2 + \text{C} \end{array} \right.$ $\rightarrow \left\{ \begin{array}{l} \text{C}_2 + {}^1\text{CH}_2 \\ \text{C}_2 + {}^3\text{CH}_2 \end{array} \right.$	$0.875 \pm 0.017$ [1, 11, 74, 75] $0.125 \pm 0.021$
$\text{c-C}_3\text{H}_3^+ + \text{e}^-$	$\rightarrow \left\{ \begin{array}{l} \text{C}_3\text{H}_2 + \text{H} \\ \text{C}_3\text{H} + \text{H}_2 \\ \text{C}_3\text{H} + 2\text{H} \\ \text{C}_3 + \text{H} + \text{H}_2 \end{array} \right.$ $\rightarrow \left\{ \begin{array}{l} \text{C}_2\text{H}_2 + \text{CH} \\ \text{C}_2\text{H}_2 + \text{C} + \text{H} \\ \text{C}_2\text{H} + {}^1\text{CH}_2 \\ \text{C}_2\text{H} + {}^3\text{CH}_2 \end{array} \right.$ $\text{C}_2 + \text{CH}_3$	$0.907 \pm 0.011$ [1, 11, 74, 75] [Note 3] $0.093 \pm 0.005$
$\text{l-C}_3\text{H}_3^+ + \text{e}^-$	$\rightarrow \left\{ \begin{array}{l} \text{C}_3\text{H}_2 + \text{H} \\ \text{C}_3\text{H} + \text{H}_2 \\ \text{C}_3\text{H} + 2\text{H} \\ \text{C}_3 + \text{H} + \text{H}_2 \end{array} \right.$ $\rightarrow \left\{ \begin{array}{l} \text{C}_2\text{H}_2 + \text{CH} \\ \text{C}_2\text{H}_2 + \text{C} + \text{H} \\ \text{C}_2\text{H} + {}^1\text{CH}_2 \\ \text{C}_2\text{H} + {}^3\text{CH}_2 \end{array} \right.$ $\text{C}_2 + \text{CH}_3$	$0.907 \pm 0.011$ [1, 11, 74, 75] [Note 3] $0.093 \pm 0.005$
$\text{C}_3\text{H}_4^+ + \text{e}^-$	$\rightarrow \text{C}_3\text{H}_3 + \text{H}$ $\rightarrow \text{C}_3\text{H}_2 + \text{H}_2$ $\rightarrow \text{C}_3\text{H}_2 + 2\text{H}$ $\rightarrow \text{C}_2\text{H}_3 + \text{CH}$ $\rightarrow \left\{ \begin{array}{l} \text{C}_2\text{H}_2 + {}^1\text{CH}_2 \\ \text{C}_2\text{H}_2 + {}^3\text{CH}_2 \end{array} \right.$	$0.87 \pm 0.04$ [1, 11, 22, 74, 75] $\leq 0.02$ $\leq 0.05$ $0.01 \pm 0.01$ $0.06 \pm 0.02$



Reaction	Products	Branching ratios
	$\rightarrow \left\{ \begin{array}{l} \text{C}_2\text{H}_5 + \text{CH} \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_4 + {}^1\text{CH}_2 \\ \text{C}_2\text{H}_4 + {}^3\text{CH}_2 \end{array} \right. \\ \text{C}_2\text{H}_4 + \text{CH} + \text{H} \\ \text{C}_2\text{H}_4 + \text{C} + \text{H}_2 \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_3 + \text{CH} + \text{H}_2 \\ \text{C}_2\text{H}_3 + \text{CH}_3 \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_2 + \text{CH}_4 \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_2 + {}^1\text{CH}_2 + \text{H}_2 \\ \text{C}_2\text{H}_2 + {}^3\text{CH}_2 + \text{H}_2 \end{array} \right. \\ \text{C}_2\text{H}_2 + \text{CH}_3 + \text{H} \\ \left\{ \begin{array}{l} \text{C}_2\text{H} + \text{CH}_4 + \text{H} \\ \text{C}_2\text{H} + \text{CH}_3 + \text{H}_2 \end{array} \right. \end{array} \right.$	$0.307 \pm 0.013$
	$\rightarrow \text{C} + \text{CH}_2 + \text{CH}_4$	$0.00 \pm 0.01$
$\text{C}_3\text{H}_7^+ + \text{e}^-$	$\rightarrow \text{C}_3\text{H}_6 + \text{H}$	$0.13 \pm 0.05$ [76] [Note 5]
	$\rightarrow \text{C}_3\text{H}_5 + \text{H}_2$	$0.12 \pm 0.05$
	$\rightarrow \text{C}_3\text{H}_5 + 2\text{H}$	$0.22 \pm 0.08$
	$\rightarrow \text{C}_3\text{H}_4 + \text{H}_2 + \text{H}$	$0.09 \pm 0.02$
	$\rightarrow \text{C}_2\text{H}_4 + \text{CH}_3$	$0.03 \pm 0.02$
	$\rightarrow \text{C}_2\text{H}_3 + \text{CH}_4$	$0.02 \pm 0.02$
	$\rightarrow \text{C}_2\text{H}_3 + \text{CH}_3 + \text{H}$	$0.15 \pm 0.04$
	$\rightarrow \text{C}_2\text{H}_2 + \text{CH}_4 + \text{H}$	$0.03 \pm 0.03$
	$\rightarrow \text{C}_2\text{H}_2 + \text{CH}_3 + \text{H}_2$	$0.21 \pm 0.04$
$\text{C}_3\text{H}_8^+ + \text{e}^-$	$\rightarrow \left\{ \begin{array}{l} \text{C}_3\text{H}_7 + \text{H} \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_6 + \text{H}_2 \\ \text{C}_3\text{H}_6 + 2\text{H} \end{array} \right. \\ \text{C}_3\text{H}_5 + \text{H}_2 + \text{H} \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_4 + 2\text{H}_2 \\ \text{C}_3\text{H}_4 + \text{H}_2 + 2\text{H} \end{array} \right. \end{array} \right.$	$0.679 \pm 0.029$ [1, 11, 74, 75]

Reaction	Products	Branching ratios
	$\rightarrow \left\{ \begin{array}{l} \left\{ \begin{array}{l} \text{C}_2\text{H}_6 + {}^1\text{CH}_2 \\ \text{C}_2\text{H}_6 + {}^3\text{CH}_2 \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_5 + \text{CH}_3 \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_5 + {}^1\text{CH}_2 + \text{H} \\ \text{C}_2\text{H}_5 + {}^3\text{CH}_2 + \text{H} \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_5 + \text{CH} + \text{H}_2 \\ \text{C}_2\text{H}_5 + \text{CH} + 2\text{H} \end{array} \right. \\ \text{C}_2\text{H}_4 + \text{CH}_4 \\ \text{C}_2\text{H}_4 + \text{CH}_3 + \text{H} \\ \left\{ \begin{array}{l} \left\{ \begin{array}{l} \text{C}_2\text{H}_4 + {}^1\text{CH}_2 + \text{H}_2 \\ \text{C}_2\text{H}_4 + {}^1\text{CH}_2 + 2\text{H} \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_4 + {}^3\text{CH}_2 + \text{H}_2 \\ \text{C}_2\text{H}_4 + {}^3\text{CH}_2 + 2\text{H} \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_3 + \text{CH}_3 + \text{H}_2 \\ \text{C}_2\text{H}_3 + \text{CH}_3 + 2\text{H} \end{array} \right. \\ \text{C}_2\text{H}_3 + \text{CH}_4 + \text{H} \\ \text{C}_2\text{H}_2 + \text{CH}_4 + \text{H}_2 \\ \text{CH}_4 + \text{CH}_3 + \text{CH} \\ \left\{ \begin{array}{l} \text{CH}_4 + {}^1\text{CH}_2 + {}^1\text{CH}_2 \\ \text{CH}_4 + {}^1\text{CH}_2 + {}^3\text{CH}_2 \\ \text{CH}_4 + {}^3\text{CH}_2 + {}^3\text{CH}_2 \\ 2\text{CH}_3 + {}^1\text{CH}_2 \\ 2\text{CH}_3 + {}^3\text{CH}_2 \end{array} \right. \end{array} \right.$	$0.321 \pm 0.028$
	$\rightarrow \left\{ \begin{array}{l} \left\{ \begin{array}{l} \text{CH}_4 + {}^1\text{CH}_2 + {}^1\text{CH}_2 \\ \text{CH}_4 + {}^1\text{CH}_2 + {}^3\text{CH}_2 \\ \text{CH}_4 + {}^3\text{CH}_2 + {}^3\text{CH}_2 \\ 2\text{CH}_3 + {}^1\text{CH}_2 \\ 2\text{CH}_3 + {}^3\text{CH}_2 \end{array} \right. \end{array} \right.$	$0.00 \pm 0.01$
$\text{C}_4\text{H}^+ + \text{e}^-$	$\rightarrow \text{C}_4 + \text{H}$	$0.439 \pm 0.012 \text{ for } \sum = 1 \text{ (0.438) [1, 75, 77]}$
	$\rightarrow \text{C}_3\text{H} + \text{C}$	$0.282 \pm 0.021$
	$\rightarrow \text{C}_2\text{H} + \text{C}_2$	$0.279 \pm 0.017$
$\text{C}_4\text{H}_2^+ + \text{e}^-$	$\rightarrow \left\{ \begin{array}{l} \text{C}_4\text{H} + \text{H} \\ \text{C}_4 + \text{H}_2 \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_2 + \text{C} \\ \text{C}_3\text{H} + \text{CH} \\ \left\{ \begin{array}{l} \text{C}_3 + {}^1\text{CH}_2 \\ \text{C}_3 + {}^3\text{CH}_2 \end{array} \right. \end{array} \right. \end{array} \right.$	$0.783 \pm 0.013 \text{ for } \sum = 1 \text{ (0.784) [1, 75, 77]}$
	$\rightarrow \left\{ \begin{array}{l} \left\{ \begin{array}{l} \text{C}_3 + {}^1\text{CH}_2 \\ \text{C}_3 + {}^3\text{CH}_2 \end{array} \right. \end{array} \right.$	$0.040 \pm 0.016$

Reaction	Products	Branching ratios
	$\rightarrow \begin{cases} \text{C}_2\text{H}_2 + \text{C}_2 \\ 2 \text{C}_2\text{H} \end{cases}$	$0.177 \pm 0.015$
$\text{C}_4\text{H}_3^+ + \text{e}^-$	$\rightarrow \begin{cases} \text{C}_4\text{H}_2 + \text{H} \\ \begin{cases} \text{C}_4\text{H} + \text{H}_2 \\ \text{C}_4\text{H} + 2 \text{H} \end{cases} \\ \text{C}_4 + \text{H} + \text{H}_2 \end{cases}$ $\rightarrow \begin{cases} \text{C}_3\text{H}_3 + \text{C} \\ \text{C}_3\text{H}_2 + \text{CH} \\ \begin{cases} \text{C}_3\text{H} + {}^1\text{CH}_2 \\ \text{C}_3\text{H} + {}^3\text{CH}_2 \end{cases} \\ \text{C}_3 + \text{CH}_3 \end{cases}$ $\rightarrow \begin{cases} \text{C}_2\text{H}_3 + \text{C}_2 \\ \text{C}_2\text{H}_2 + \text{C}_2\text{H} \end{cases}$	$0.759 \pm 0.005$ for $\Sigma = 1$ (0.760) [1, 75, 77]  $0.063 \pm 0.004$  $0.178 \pm 0.004$
$\text{C}_4\text{H}_4^+ + \text{e}^-$	$\rightarrow \begin{cases} \text{C}_4\text{H}_3 + \text{H} \\ \begin{cases} \text{C}_4\text{H}_2 + \text{H}_2 \\ \text{C}_4\text{H}_2 + 2 \text{H} \end{cases} \\ \text{C}_4\text{H} + \text{H}_2 + \text{H} \end{cases}$ $\rightarrow \begin{cases} \text{C}_3\text{H}_4 + \text{C} \\ \text{C}_3\text{H}_3 + \text{CH} \\ \begin{cases} \begin{cases} \text{C}_3\text{H}_2 + {}^1\text{CH}_2 \\ \text{C}_3\text{H}_2 + {}^3\text{CH}_2 \end{cases} \\ \text{C}_3\text{H}_2 + \text{C} + \text{H}_2 \end{cases} \\ \text{C}_3\text{H} + \text{CH}_3 \\ \begin{cases} \text{C}_3 + \text{CH}_4 \\ \text{C}_3 + \text{CH}_3 + \text{H} \end{cases} \end{cases}$ $\rightarrow \begin{cases} \text{C}_2\text{H}_4 + \text{C}_2 \\ \text{C}_2\text{H}_3 + \text{C}_2\text{H} \\ \begin{cases} 2 \text{C}_2\text{H}_2 \\ \text{C}_2\text{H}_2 + \text{C}_2\text{H} + \text{H} \\ \text{C}_2\text{H}_2 + \text{C}_2 + \text{H}_2 \end{cases} \\ 2 \text{C}_2\text{H} + \text{H}_2 \end{cases}$	$0.766 \pm 0.027$ [1, 75, 77]   $0.063 \pm 0.02$       $0.171 \pm 0.021$

Reaction	Products	Branching ratios
$\text{C}_4\text{H}_5^+ + \text{e}^-$	$\rightarrow \left\{ \begin{array}{l} \text{C}_4\text{H}_4 + \text{H} \\ \left\{ \begin{array}{l} \text{C}_4\text{H}_3 + \text{H}_2 \\ \text{C}_4\text{H}_3 + 2 \text{H} \end{array} \right. \\ \text{C}_4\text{H}_2 + \text{H}_2 + \text{H} \\ \text{C}_4\text{H} + 2 \text{H}_2 \end{array} \right.$	$0.460 \pm 0.054$ [1, 75, 77]
	$\rightarrow \left\{ \begin{array}{l} \text{C}_3\text{H}_5 + \text{C} \\ \text{C}_3\text{H}_4 + \text{CH} \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_3 + {}^1\text{CH}_2 \\ \text{C}_3\text{H}_3 + {}^3\text{CH}_2 \end{array} \right. \\ \text{C}_3\text{H}_2 + \text{CH}_3 \\ \text{C}_3\text{H} + \text{CH}_4 \end{array} \right.$	
	$\rightarrow \left\{ \begin{array}{l} \text{C}_2\text{H}_5 + \text{C}_2 \\ \text{C}_2\text{H}_4 + \text{C}_2\text{H} \\ \text{C}_2\text{H}_3 + \text{C}_2\text{H}_2 \\ \left\{ \begin{array}{l} 2 \text{C}_2\text{H}_2 + \text{H} \\ \text{C}_2\text{H}_2 + \text{C}_2\text{H} + \text{H}_2 \end{array} \right. \end{array} \right.$	
$\text{C}_4\text{H}_6^+ + \text{e}^-$	$\rightarrow \left\{ \begin{array}{l} \text{C}_4\text{H}_5 + \text{H} \\ \left\{ \begin{array}{l} \text{C}_4\text{H}_4 + \text{H}_2 \\ \text{C}_4\text{H}_4 + 2 \text{H} \end{array} \right. \\ \text{C}_4\text{H}_3 + \text{H}_2 + \text{H} \\ \left\{ \begin{array}{l} \text{C}_4\text{H}_2 + 2 \text{H}_2 \\ \text{C}_4\text{H}_2 + \text{H}_2 + 2 \text{H} \end{array} \right. \end{array} \right.$	$0.589 \pm 0.035$ [1, 75, 77]

Reaction	Products	Branching ratios
	$\rightarrow \left\{ \begin{array}{l} \text{C}_3\text{H}_6 + \text{C} \\ \text{C}_3\text{H}_5 + \text{CH} \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_4 + {}^1\text{CH}_2 \\ \text{C}_3\text{H}_4 + {}^3\text{CH}_2 \end{array} \right. \\ \text{C}_3\text{H}_4 + \text{C} + \text{H}_2 \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_3 + \text{CH}_3 \\ \text{C}_3\text{H}_3 + \text{CH} + \text{H}_2 \end{array} \right. \end{array} \right.$	$0.090 \pm 0.015$
	$\rightarrow \left\{ \begin{array}{l} \text{C}_3\text{H}_2 + \text{CH}_4 \\ \text{C}_3\text{H}_2 + \text{CH}_3 + \text{H} \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_2 + {}^1\text{CH}_2 + \text{H}_2 \\ \text{C}_3\text{H}_2 + {}^3\text{CH}_2 + \text{H}_2 \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_3\text{H} + \text{CH}_4 + \text{H} \\ \text{C}_3\text{H} + \text{CH}_3 + \text{H}_2 \end{array} \right. \end{array} \right.$	
	$\rightarrow \left\{ \begin{array}{l} \text{C}_2\text{H}_6 + \text{C}_2 \\ \text{C}_2\text{H}_5 + \text{C}_2\text{H} \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_4 + \text{C}_2\text{H} + \text{H} \\ \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2 \\ \text{C}_2\text{H}_4 + \text{C}_2 + \text{H}_2 \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_3 + \text{C}_2\text{H}_2 + \text{H} \\ \text{C}_2\text{H}_3 + \text{C}_2\text{H} + \text{H}_2 \end{array} \right. \end{array} \right.$	$0.321 \pm 0.034$
	$\rightarrow \left\{ \begin{array}{l} \text{C}_2\text{H}_2 + \text{CH} + \text{CH}_3 \\ \text{C}_2\text{H}_2 + \text{C} + \text{CH}_4 \end{array} \right.$	$0.00 \pm 0.01$
$\text{C}_4\text{H}_7^+ + \text{e}^-$	$\rightarrow \left\{ \begin{array}{l} \text{C}_4\text{H}_6 + \text{H} \\ \left\{ \begin{array}{l} \text{C}_4\text{H}_5 + \text{H}_2 \\ \text{C}_4\text{H}_5 + 2\text{H} \end{array} \right. \\ \text{C}_4\text{H}_4 + \text{H}_2 + \text{H} \\ \text{C}_4\text{H}_3 + 2\text{H}_2 \end{array} \right.$	$0.198 \pm 0.044$ [1, 75, 77]

Reaction	Products	Branching ratios
	$\rightarrow \left\{ \begin{array}{l} \text{C}_3\text{H}_7 + \text{C} \\ \text{C}_3\text{H}_6 + \text{CH} \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_5 + {}^1\text{CH}_2 \\ \text{C}_3\text{H}_5 + {}^3\text{CH}_2 \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_4 + \text{CH}_3 \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_4 + {}^1\text{CH}_2 + \text{H} \\ \text{C}_3\text{H}_4 + {}^3\text{CH}_2 + \text{H} \end{array} \right. \\ \text{C}_3\text{H}_4 + \text{CH} + \text{H}_2 \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_3 + \text{CH}_4 \\ \text{C}_3\text{H}_3 + \text{CH}_3 + \text{H} \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_3 + {}^1\text{CH}_2 + \text{H}_2 \\ \text{C}_3\text{H}_3 + {}^3\text{CH}_2 + \text{H}_2 \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_2 + \text{CH}_4 + \text{H} \\ \text{C}_3\text{H}_2 + \text{CH}_3 + \text{H}_2 \end{array} \right. \\ \text{C}_3\text{H} + \text{CH}_4 + \text{H}_2 \end{array} \right.$	$0.655 \pm 0.059$
	$\rightarrow \left\{ \begin{array}{l} \text{C}_2\text{H}_6 + \text{C}_2\text{H} \\ \text{C}_2\text{H}_5 + \text{C}_2\text{H}_2 \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2 + \text{H} \\ \text{C}_2\text{H}_4 + \text{C}_2\text{H} + \text{H}_2 \end{array} \right. \\ \left\{ \begin{array}{l} 2\text{C}_2\text{H}_3 + \text{H} \\ \text{C}_2\text{H}_3 + \text{C}_2\text{H}_2 + \text{H}_2 \end{array} \right. \end{array} \right.$	$0.147 \pm 0.034$
	$\rightarrow \left\{ \begin{array}{l} \text{C}_2\text{H}_2 + {}^1\text{CH}_2 + \text{CH}_3 \\ \text{C}_2\text{H}_2 + {}^3\text{CH}_2 + \text{CH}_3 \end{array} \right.$	$0.00 \pm 0.01$
$\text{C}_4\text{H}_8^+ + \text{e}^-$	$\rightarrow \left\{ \begin{array}{l} \text{C}_4\text{H}_7 + \text{H} \\ \left\{ \begin{array}{l} \text{C}_4\text{H}_6 + \text{H}_2 \\ \text{C}_4\text{H}_6 + 2\text{H} \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_4\text{H}_5 + \text{H}_2 + \text{H} \\ \text{C}_4\text{H}_5 + 3\text{H} \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_4\text{H}_4 + 2\text{H}_2 \\ \text{C}_4\text{H}_4 + \text{H}_2 + 2\text{H} \end{array} \right. \end{array} \right.$	$0.305 \pm 0.031$ [1, 75, 77]





Reaction	Products	Branching ratios
	$\rightarrow \left\{ \begin{array}{l} \left\{ \begin{array}{l} \text{C}_2\text{H}_4 + \text{CH} + \text{CH}_3 \\ \text{C}_2\text{H}_4 + \text{C} + \text{CH}_4 \end{array} \right. \\ \text{C}_2\text{H}_3 + \text{CH} + \text{CH}_4 \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_2 + 2 \text{CH}_3 \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_2 + {}^1\text{CH}_2 + \text{CH}_4 \\ \text{C}_2\text{H}_2 + {}^3\text{CH}_2 + \text{CH}_4 \end{array} \right. \end{array} \right. \\ \text{C}_2\text{H} + \text{CH}_4 + \text{CH}_3 \\ \text{C}_2 + 2 \text{CH}_4 \end{array} \right.$	$0.000 \pm 0.010$
$\text{C}_4\text{H}_9^+ + \text{e}^-$	$\rightarrow \left\{ \begin{array}{l} \text{C}_4\text{H}_8 + \text{H} \\ \left\{ \begin{array}{l} \text{C}_4\text{H}_7 + \text{H}_2 \\ \text{C}_4\text{H}_7 + 2 \text{H} \end{array} \right. \\ \text{C}_4\text{H}_6 + \text{H}_2 + \text{H} \\ \left\{ \begin{array}{l} \text{C}_4\text{H}_5 + 2 \text{H}_2 \\ \text{C}_4\text{H}_5 + \text{H}_2 + 2 \text{H} \end{array} \right. \end{array} \right.$	$0.574 \pm 0.041$ for $\sum = 1$ (0.575) [1, 75, 77, 78]
	$\rightarrow \left\{ \begin{array}{l} \text{C}_3\text{H}_8 + \text{CH} \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_7 + {}^1\text{CH}_2 \\ \text{C}_3\text{H}_7 + {}^3\text{CH}_2 \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_6 + \text{CH}_3 \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_6 + {}^1\text{CH}_2 + \text{H} \\ \text{C}_3\text{H}_6 + {}^3\text{CH}_2 + \text{H} \end{array} \right. \end{array} \right. \\ \text{C}_3\text{H}_6 + \text{CH} + \text{H}_2 \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_5 + \text{CH}_4 \\ \text{C}_3\text{H}_5 + \text{CH}_3 + \text{H} \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_5 + {}^1\text{CH}_2 + \text{H}_2 \\ \text{C}_3\text{H}_5 + {}^3\text{CH}_2 + \text{H}_2 \end{array} \right. \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_4 + \text{CH}_4 + \text{H} \\ \text{C}_3\text{H}_4 + \text{CH}_3 + \text{H}_2 \end{array} \right. \\ \text{C}_3\text{H}_3 + \text{CH}_4 + \text{H}_2 \end{array} \right.$	$0.411 \pm 0.038$

Reaction	Products	Branching ratios
	$\rightarrow \left\{ \begin{array}{l} \left\{ \begin{array}{l} \text{C}_2\text{H}_6 + \text{C}_2\text{H}_3 \\ \text{C}_2\text{H}_6 + \text{C}_2\text{H}_2 + \text{H} \\ \text{C}_2\text{H}_6 + \text{C}_2\text{H} + \text{H}_2 \\ \text{C}_2\text{H}_5 + \text{C}_2\text{H}_4 \\ \text{C}_2\text{H}_5 + \text{C}_2\text{H}_3 + \text{H} \\ \text{C}_2\text{H}_5 + \text{C}_2\text{H}_2 + \text{H}_2 \end{array} \right. \\ 2 \text{C}_2\text{H}_4 + \text{H} \end{array} \right.$	$0.015 \pm 0.026$
	$\rightarrow \left\{ \begin{array}{l} \left\{ \begin{array}{l} \text{C}_2\text{H}_4 + \text{CH} + \text{CH}_4 \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_4 + {}^1\text{CH}_2 + \text{CH}_3 \\ \text{C}_2\text{H}_4 + {}^3\text{CH}_2 + \text{CH}_3 \end{array} \right. \\ \text{C}_2\text{H}_3 + 2 \text{CH}_3 \\ \left\{ \begin{array}{l} \text{C}_2\text{H}_3 + {}^1\text{CH}_2 + \text{CH}_4 \\ \text{C}_2\text{H}_3 + {}^3\text{CH}_2 + \text{CH}_4 \end{array} \right. \\ \text{C}_2\text{H}_2 + \text{CH}_3 + \text{CH}_4 \end{array} \right.$	$0.000 \pm 0.010$
$\text{N}^+ + \text{e}^-$	$\rightarrow \text{N} + \text{h}\nu$	-
$\text{NH}^+ + \text{e}^-$	$\rightarrow \text{N} + \text{H}$	-
$\text{NH}_2^+ + \text{e}^-$	$\rightarrow \text{N} + \text{H}_2$	$0.04 \pm 0.03$ [79, 80]
	$\rightarrow \text{NH} + \text{H}$	$0.38 \pm 0.06$ [Note 6]
	$\rightarrow \left\{ \begin{array}{l} ({}^4S)\text{N} + 2 \text{H} \\ ({}^2D)\text{N} + 2 \text{H} \\ ({}^2P)\text{N} + 2 \text{H} \end{array} \right.$	$0.58 \pm 0.09 \left\{ \begin{array}{l} 0.53 \pm 0.04 \\ 0.45 \pm 0.05 \\ 0.02 \pm 0.02 \end{array} \right.$
$\text{NH}_3^+ + \text{e}^-$	$\rightarrow \left\{ \begin{array}{l} \text{NH}_2 + \text{H} \\ \left\{ \begin{array}{l} \text{NH} + \text{H}_2 \\ \text{NH} + 2 \text{H} \\ \text{N} + \text{H}_2 + \text{H} \\ \text{N} + 3 \text{H} \end{array} \right. \end{array} \right.$	Exoergic channels
$\text{NH}_4^+ + \text{e}^-$	$\rightarrow \text{NH}_3 + \text{H}$	$0.85 \pm 0.04$ [20, 29, 79, 81]
	$\rightarrow \text{NH}_2 + \text{H}_2$	$0.2 \pm 0.02$
	$\rightarrow \text{NH}_2 + 2\text{H}$	$0.13 \pm 0.01$
	$\rightarrow \text{NH} + \text{H} + \text{H}_2$	$0.00 \pm 0.01$
	$\rightarrow \text{N} + 2\text{H}_2$	$0.00 \pm 0.01$
$\text{N}_2^+ + \text{e}^-$	$\rightarrow ({}^4S)\text{N} + ({}^2D)\text{N}$	$0.42 \pm 0.10$ [37, 82]

Reaction	Products	Branching ratios
	$\rightarrow (^4S)N + (^2P)N$	$0.09 \pm 0.09$
	$\rightarrow (^2D)N + (^2D)N$	$0.49 \pm 0.10$
$N_2H^+ + e^-$	$\rightarrow N_2 + H$	0.95-1 [13, 70, 83]
	$\rightarrow NH + N$	0-0.05
$CN^+ + e^-$	$\rightarrow (^4S)N + (^3P)C$	$\leq 0.018$ [44] [Note 7]
	$\rightarrow (^4S)N + (^1D)C$	$0.038 \pm 0.028$
	$\rightarrow \begin{cases} (^2D)N + (^3P)C \\ (^4S)N + (^1S)C \end{cases}$	$0.142 \pm 0.014$
	$\rightarrow \begin{cases} (^2P)N + (^3P)C \\ (^2D)N + (^1D)C \end{cases}$	$0.561 \pm 0.026$
	$\rightarrow \begin{cases} (^2P)N + (^1D)C \\ (^2D)N + (^1S)C \end{cases}$	$0.255 \pm 0.014$
	$\rightarrow (^2P)N + (^1S)C$	$\leq 0.014$
$HCN^+ + e^-$	$\rightarrow CN + H$	-
$HNC^+ + e^-$	$\rightarrow CN + H$	-
$HCNH^+ + e^-$	$\rightarrow HCN + H$	0.26-0.41 [47, 84, 85] [Note 2]
	$\rightarrow HNC + H$	0.29-0.39 [47, 84, 85]
	$\rightarrow CN + H_2$	$0 \pm 0.017$ [47]
	$\rightarrow CN + 2H$	$0.325 \pm 0.032$ [47]
$CH_2NH_2^+ + e^-$	$\rightarrow \begin{cases} CH_3N + H \\ \begin{cases} ^1CH_2 + NH_2 \\ ^3CH_2 + NH_2 \end{cases} \\ \begin{cases} HCN + H_2 + H \\ HNC + H_2 + H \end{cases} \\ CN + 2H_2 \end{cases}$	Exoergic channels
$CH_3CNH^+ + e^-$	$\rightarrow \begin{cases} a \begin{cases} CH_3CN + H \\ \begin{cases} C_2H_2N + H_2 \\ C_2H_2N + 2H \end{cases} \\ C_2HN + H_2 + H \end{cases} \\ b \ C_2N + 2H_2 \end{cases}$	$0.65 \pm 0.03$ , $a \in [0.25, 1]$ , $b \in [0, 0.25]$ [68] [Note 5]

Reaction	Products	Branching ratios
	$\rightarrow \left\{ \begin{array}{l} c \left\{ \begin{array}{l} \text{C}_2\text{H}_4 + \text{N} \\ \text{C}_2\text{H}_2 + \text{NH}_2 \\ \text{C}_2\text{H}_2 + \text{NH} + \text{H} \\ \text{C}_2\text{H}_2 + \text{N} + \text{H}_2 \\ \text{C}_2\text{H} + \text{NH}_3 \\ \text{C}_2\text{H} + \text{NH} + \text{H}_2 \end{array} \right. \\ e \left\{ \begin{array}{l} \left\{ \begin{array}{l} \text{HCN} + \text{CH}_3 \\ \text{HNC} + \text{CH}_3 \end{array} \right. \\ \left\{ \begin{array}{l} \text{HCN} + {}^1\text{CH}_2 + \text{H} \\ \text{HCN} + {}^3\text{CH}_2 + \text{H} \end{array} \right. \\ \left\{ \begin{array}{l} \text{HNC} + {}^1\text{CH}_2 + \text{H} \\ \text{HNC} + {}^3\text{CH}_2 + \text{H} \end{array} \right. \\ \left\{ \begin{array}{l} \text{HCN} + \text{CH} + \text{H}_2 \\ \text{HNC} + \text{CH} + \text{H}_2 \end{array} \right. \\ \text{CN} + \text{CH}_3 + \text{H} \end{array} \right. \\ d \left\{ \begin{array}{l} \text{CH}_3\text{N} + \text{CH} \\ \left\{ \begin{array}{l} \text{CH}_2\text{N} + {}^1\text{CH}_2 \\ \text{CH}_2\text{N} + {}^3\text{CH}_2 \end{array} \right. \\ \text{CN} + \text{CH}_4 \\ \left\{ \begin{array}{l} \text{CN} + {}^1\text{CH}_2 + \text{H}_2 \\ \text{CN} + {}^3\text{CH}_2 + \text{H}_2 \end{array} \right. \end{array} \right. \\ f \left\{ \begin{array}{l} \text{CH}_3\text{N} + \text{CH} \\ \left\{ \begin{array}{l} \text{CH}_2\text{N} + {}^1\text{CH}_2 \\ \text{CH}_2\text{N} + {}^3\text{CH}_2 \end{array} \right. \\ \text{CN} + \text{CH}_4 \\ \left\{ \begin{array}{l} \text{CN} + {}^1\text{CH}_2 + \text{H}_2 \\ \text{CN} + {}^3\text{CH}_2 + \text{H}_2 \end{array} \right. \end{array} \right. \end{array} \right.$	$0.35 \pm 0.03, d \geq c, e \geq f$
$\text{C}_2\text{N}_2^+ + \text{e}^-$	$\rightarrow 2 \text{CN}$	- [86]
$\text{C}_3\text{N}^+ + \text{e}^-$	$\rightarrow \text{CN} + \text{C}_2$	- [9]
$\text{CHCCN}^+ + \text{e}^-$	$\rightarrow \text{C}_3\text{N} + \text{H}$	$0.44 \pm 0.04$ [87] [Note 5]
	$\rightarrow \left\{ \begin{array}{l} \text{C}_2\text{H} + \text{CN} \\ \text{C}_2 + \text{H} + \text{CN} \\ \left\{ \begin{array}{l} \text{HCN} + \text{C}_2 \\ \text{HNC} + \text{C}_2 \end{array} \right. \end{array} \right.$	$0.48 \pm 0.05$
	$\rightarrow \text{H} + \text{C} + \text{C}_2\text{N}$	$0.04 \pm 0.02$
	$\rightarrow \left\{ \begin{array}{l} \text{C}_2\text{N} + \text{CH} \\ \text{N} + \text{C}_3\text{H} \end{array} \right.$	$0.02 \pm 0.01$
	$\rightarrow \text{HC}_2\text{N} + \text{C}$	$0.02 \pm 0.01$

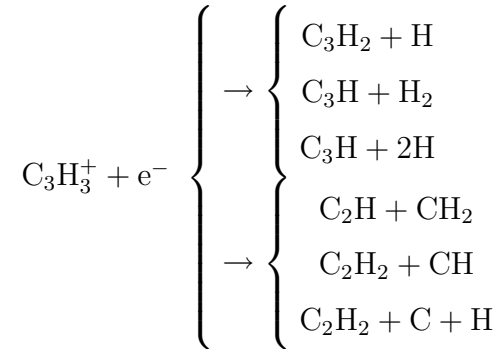
Reaction	Products	Branching ratios
	$\rightarrow \text{NH} + \text{C}_3$	$0.00 \pm 0.01$
$\text{CHCCNH}^+ + \text{e}^-$	$\rightarrow \left\{ \begin{array}{l} \left\{ \begin{array}{l} \text{HC}_3\text{N} + \text{H} \\ \text{C}_3\text{NH} + \text{H} \end{array} \right. \\ \left\{ \begin{array}{l} \text{C}_2\text{NCH} + \text{H} \\ \text{HC}_2\text{NC} + \text{H} \end{array} \right. \end{array} \right.$	$0.52 \pm 0.05, a \geq b$ [88, 89] [Note 5]
	$\rightarrow \left\{ \begin{array}{l} \text{C}_3\text{N} + \text{H}_2 \\ \left\{ \begin{array}{l} \text{HNC} + \text{C}_2\text{H} \\ \text{HCN} + \text{C}_2\text{H} \end{array} \right. \\ \text{CN} + \text{C}_2\text{H}_2 \end{array} \right.$	$0.48 \pm 0.05$
$\text{CH}_2\text{CHCNH}^+ + \text{e}^-$	$\rightarrow \left\{ \begin{array}{l} \text{C}_3\text{H}_3\text{N} + \text{H} \\ \left\{ \begin{array}{l} \text{C}_3\text{H}_2\text{N} + \text{H}_2 \\ \text{C}_3\text{H}_2\text{N} + 2\text{H} \end{array} \right. \\ \text{C}_3\text{HN} + \text{H} + \text{H}_2 \\ \left\{ \begin{array}{l} \text{C}_3\text{N} + 2\text{H}_2 \\ \text{C}_3\text{N} + 2\text{H} + \text{H}_2 \end{array} \right. \end{array} \right.$	$0.50 \pm 0.04$ [50] [Note 5]
	$\rightarrow \left\{ \begin{array}{l} \text{CNH}_3 + \text{C}_2\text{H} \\ \text{CNH}_2 + \text{C}_2\text{H}_2 \\ \left\{ \begin{array}{l} \text{HCN} + \text{C}_2\text{H}_3 \\ \text{HNC} + \text{C}_2\text{H}_3 \end{array} \right. \\ \left\{ \begin{array}{l} \text{HCN} + \text{C}_2\text{H}_2 + \text{H} \\ \text{HNC} + \text{C}_2\text{H}_2 + \text{H} \end{array} \right. \\ \left\{ \begin{array}{l} \text{HCN} + \text{C}_2\text{H} + \text{H}_2 \\ \text{HNC} + \text{C}_2\text{H} + \text{H}_2 \end{array} \right. \\ \text{CN} + \text{C}_2\text{H}_4 \\ \text{CN} + \text{C}_2\text{H}_2 + \text{H}_2 \end{array} \right.$	$0.49 \pm 0.04$

Reaction	Products	Branching ratios
	$\rightarrow \left\{ \begin{array}{l} \text{C}_2\text{H}_3\text{N} + \text{CH} \\ \text{C}_2\text{H}_2\text{N} + {}^1\text{CH}_2 \\ \text{C}_2\text{H}_2\text{N} + {}^3\text{CH}_2 \\ \text{C}_2\text{HN} + \text{CH}_3 \\ \text{C}_2\text{N} + \text{CH}_4 \\ \text{C}_2\text{N} + \text{CH}_3 + \text{H} \\ \text{NH}_3 + \text{C}_3\text{H} \\ \text{NH}_2 + \text{C}_3\text{H}_2 \\ \text{NH} + \text{C}_3\text{H}_3 \\ \text{N} + \text{C}_3\text{H}_4 \end{array} \right.$	$0.01 \pm 0.01$
$\text{H}_2\text{O}^+ + \text{e}^-$	$\rightarrow \text{OH} + \text{H}$	$0.25 \pm 0.1$ [52, 53, 69, 90]
	$\rightarrow \text{O} + \text{H}_2$	$0.10 \pm 0.06$
	$\rightarrow \text{O} + 2\text{H}$	$0.65 \pm 0.1$
$\text{H}_3\text{O}^+ + \text{e}^-$	$\rightarrow \text{OH} + 2\text{H}$	$0.60 \pm 0.15$ [55, 56, 69, 91, 92] [Note 8]
	$\rightarrow \text{H}_2\text{O} + \text{H}$	$0.25 \pm 0.05$
	$\rightarrow \text{OH} + \text{H}_2$	$0.14 \pm 0.05$
	$\rightarrow \text{O} + \text{H}_2 + \text{H}$	$0.01 \pm 0.05$
$\text{CO}^+ + \text{e}^-$	$\rightarrow \text{C} + \text{O}$	-
$\text{HCO}^+ + \text{e}^-$	$\rightarrow \text{CO} + \text{H}$	$0.92 \pm 0.03$ [42, 81]
	$\rightarrow \text{C} + \text{OH}$	$0.07 \pm 0.02$
	$\rightarrow \text{O} + \text{CH}$	$0.01 \pm 0.01$
$\text{NO}^+ + \text{e}^-$	$\rightarrow ({}^4\text{S})\text{N} + ({}^3\text{P})\text{O}$	$0.85 \pm 0.06$ [69, 93]
	$\rightarrow \left\{ \begin{array}{l} ({}^4\text{S})\text{N} + ({}^1\text{D})\text{O} \\ ({}^2\text{D})\text{N} + ({}^3\text{D})\text{O} \end{array} \right.$	$0.15 \pm 0.06$ [69]
$\text{OH}^+ + \text{e}^-$	$\rightarrow \text{O} + \text{H}$	-

### 1. Notes for branching ratios

1. Sometimes the values of the branching ratios do not exactly add up to unity. In this case the highest value is adapted for the sum constrain. This change is specified when necessary, the measured value is given in parenthesis.

2.  $\text{HCNH}^+$ : The available data are for the ratio and the sum of the two species HNC and HCN. The ratio is characterized by  $(0.77 \leq \frac{[\text{HCN}]}{[\text{HNC}]} \leq 1.32)$ [85] and the sum by  $(\text{HCN} + \text{HNC} = 0.675 \pm 0.016)$ [47]. The values given in the database have been estimated from a Monte Carlo propagation with the former equations; they are in agreement with calculations,[84] and no further spreading of the branching ratios was necessary.
3.  $\text{l,c-C}_3\text{H}_3^+$ : the measurements of the  $\text{C}_3\text{H}_3^+$  dissociative recombination rate and branching ratios are difficult to translate into a database. Mv Lain *et al.* [21] give two different global rate constants for the l,c species, but the branching ratios only for the global form  $\text{C}_3\text{H}_3^+$  of the species. Angelova *et al.* [74] give the branching ratios as follows: “We find that the most probable channel for the recombination of  $\text{C}_3\text{H}_3^+$  is the  $\text{C}_3$  channel accounting for 90.7% of the total. This channel corresponds to the loss of a single hydrogen atom or to the loss of a  $\text{H}_2$  molecule from the cyclic ion. The linear ion, if recombining, can also lose two separate H atoms. The  $\text{C}_2 + \text{C}$  channel is not negligible, and accounts either for a unique C–C bond break in the linear ion, or for ring opening in the cyclic ion. In this case, two C–C bonds must be broken, or considerable rearrangement must occur prior to splitting.” Florescu-Mitchell and Mitchell [1] translate this information to



We accepted here that each isomer gives all the channels, even though this is probably not what is actually happening.

4. There is an actual controversy over  $\text{CH}_5^+$ , indeed Molek *et al.* [70] found values totally different from the previous experiment by Semaniak *et al.* [16]:

Reaction	Products	Branching ratios	
		FAEI [70]	CRYRING [16]
$\text{CH}_5^+ + \text{e}^- \rightarrow$	$\text{CH}_4 + \text{H}$	$95 \pm 5\%$	$4.9 \pm 1.3\%$
	$\rightarrow \text{CH}_3 + \text{H}_2$	(a)	$4.8 \pm 0.2\%$
	$\rightarrow \text{CH}_3 + 2\text{H}$	(b); (a) + (b) $\leq 8\%$	$69.8 \pm 0.8\%$
	$\rightarrow \text{CH}_2 + \text{H} + \text{H}_2$	$\leq 1\%$	$17.2 \pm 1.6\%$
	$\rightarrow \text{CH} + \text{H}_2 + \text{H}_2$	$\leq 1\%$	$3.3 \pm 1.1\%$



"The reasons for this difference are not understood at present and need more investigation in both the FA and SR." (from Ref. [70]). The CRYRING values for the branching ratios are taken at a null center-of-mass energy.

5. The neutral products and branching ratios are directly transposed from the values for deuterated ions. Geppert *et al.* [72] measured the branching ratios for the DR of  $\text{C}_2\text{D}_5^+$ , Vigren *et al.* [68] for the DR of  $\text{CD}_3\text{CND}^+$ , and Geppert *et al.* [87] for  $\text{DCCCN}^+$  and  $\text{DCCCND}^+$ , which completes calculation for the DR of  $\text{CHCCNH}^+$ . [88] Larsson *et al.* [24] discuss the comparison of  $\text{C}_3\text{H}_7^+$  and  $\text{C}_3\text{D}_7^+$  dissociative recombination branching ratios.
6.  $\text{N}_2\text{H}^+$ : [40, 42] give from CRYRING results a branching ratio of *circa*  $\frac{2}{3}$  for the  $\text{NH} + \text{H}$  channels. However, [70, 83] suspect the parasitic reaction  $^{15}\text{N}^{14}\text{N} + \text{e}^- \rightarrow ^{15}\text{N} + ^{14}\text{N}$  and a detection of  $^{15}\text{N}$  to be the reason for a measurement of so high a value for the  $\text{NH}$  channel.
7.  $\text{CN}^+$ : the different spin states of the carbon atom are given, even though the differentiation is not made in the model.
8.  $\text{H}_3\text{O}^+$ : Ref. [94] provides branching ratios in contradiction with the other measurements, they were not taken into account.

### C. Thermodynamical data

For a given DR reaction



The reaction enthalpy is given by

$$\begin{aligned} \Delta_r H^0 &= (\Delta_r H^0(\text{B}) + \Delta_r H^0(\text{C})) - \Delta_f H^0(\text{A}^+) \\ &= (\Delta_r H^0(\text{B}) + \Delta_r H^0(\text{C})) - (\Delta_f H^0(\text{A}) + \text{EI}(\text{A})) \end{aligned} \quad (3)$$

with  $\text{EI}(\text{A})$  being the ionisation energy of neutral molecule A. [95]

A channel is exoergic if  $\Delta_r H^0$  is negative.

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