$$HC_5NH^+ + e^- \rightarrow C_5N + H_2 \quad (1a)$$
$$\rightarrow HC_5N + H \quad (1b)$$
$$\rightarrow C_5NH + H \quad (1c)$$
$$\rightarrow HCN + HC_4 \quad (1d)$$
$$\rightarrow HNC + HC_4 \quad (1e)$$
$$\rightarrow HC_4N + HC \quad (1f)$$
$$\rightarrow HC_3N + HC_2 \quad (1g)$$
$$\rightarrow HC_2N + HC_3 \quad (1h)$$
$$\rightarrow H_2C_5 + N \quad (1i)$$

Thermodynamic Data

$\Delta H^o_{298}(1a) \approx -335$ kJ mol^{-1}

$\Delta H^o_{298}(1b) \approx -539$ kJ mol^{-1}

$\Delta H^o_{298}(1c) \approx -158$ kJ mol^{-1}

$\Delta H^o_{298}(1d) \approx -318$ kJ mol^{-1}

$\Delta H^o_{298}(1e) \approx -247$ kJ mol^{-1}

$\Delta H^o_{298}(1f) \approx -27$ kJ mol^{-1}

$\Delta H^o_{298}(1g) \approx -264$ kJ mol^{-1}

$\Delta H^o_{298}(1h) \approx +4$ kJ mol^{-1}

$\Delta H^o_{298}(1i) \approx -9$ kJ mol^{-1}

The enthalpy of formation of the HC_5NH^+, C_5N HC_5N, HC_3, HC_2, HC, C_5NH and HC_4 were taken from Ref. [1]. The other enthalpies of formations were obtained from the NIST webbook [2] and Ref. [3]. Reaction 1(f) and 1(h) are almost thermoneutral, errors in the determination of the ΔH^o_{298} values and the presence of barriers could affect the feasibility of these channels.

Rate Coefficient Data *k*

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
Rate Coefficient Measurements			
None			
Rate Coefficient Reviews and Evaluations			
$3.0 \times 10^{-7}(T/300)^{-0.5}$	10 – 300	UMIST database	
$3.0 \times 10^{-7}(T/300)^{-0.5}$		OSU website	

Branching Fraction Measurements

None

Branching Fraction Reviews and Evaluations

1(a) = 0.5	10 – 300	UMIST database and OSU website
1(b) = 0.5		
1(c) = 0.0		
1(d) = 0.0		

Comments

There are several isomers existing for $C_5H_2N^+$, even cyclic species are possible. Due to their interstellar significance, I restrict the following discussion to the linear ones. Three isomers of those have been discussed in the literature, and theoretical calculations yielded that the one with two hydrogen atoms on each terminal hydrogen ($HCCCNH^+$) is the most stable one with a (comparatively high) formation enthalpy of 1258 kJ/mol. [1]

With help of the data from the dissociative recombination of the lighter homologous protonated nitrile DC_3ND^+ [4] and the protonated acrylonitrile ($C_2H_3CNH^+$) [5] it might be possible to make a guess about the rate constant and branching fractions of the title reaction.

The rate constants of longer nitriles lie around 1.5×10^{-6} cm^3 $molecule^{-1}$ s^{-1} at 300 K and are therefore quite higher than the one measured for $HCNH^+$ [6]. Since there is a trend for dissociative recombination reactions to get faster with increasing complexity of the ion, one could expect a rate constant of $2.0 \times 10^{-6}(T/300)^{-0.7}cm^3$ $molecule^{-1}$ s^{-1} for the dissociative recombination of HC_5NH^+, which we recommend. Also dissociative recombination rate constants of nitriles tend to have higher temperature dependences, therefore we propose an exponential factor of -0.7.

Regarding branching fractions it has to been observed for DC_3ND^+ and $C_2H_3CNH^+$ that in around 50 % of the dissociative recombination events the carbon-nitrogen-chain stays intact. So we assume a similar behaviour for HC_5NH^+. However, it was not possible to distinguish between the different individual reaction pathways preserving the carbon chain in the named studies on protonated nitriles. We, however, assume that a hydrogen migration from one end to the other (although not impossible), only plays a minor role, therefore the branching fraction of reaction (1a) should not amount to much more than 0.04. The other processes leaving the bonds between the heavy atoms unbroken could have equal probability, so we estimate the branching fractions of (1b) and (1c) to 0.23. We further predict that reaction (1f), (1h) and (1i) do not happen, since breakages of multiple bonds were not observed in the dissociative recombination of DC_3ND^+ and $C_2H_3CNH^+$ [4,5]. There remain now three pathways breaking the carbon-nitrogen skeleton, (1d), (1e) and (1g). Again, we ascribe (1g) a minor importance (branching fraction 0.06) because of the necessity of a hydrogen migration, albeit only over 3 atoms. The distribution between (1d) and (1e) should be fairly equal (branching fraction 0.22), since the recombination process (1e) (that avoids hydrogen migration and might be favoured) very probably produces highly excited HNC, which can rearrange to the more stable HCN. The barrier of this conversion has been calculated as 129 kJ/mol [7], which is clearly inferior to the reaction enthalpy of (1e).

Preferred Values

Recommended rate constant:
$k = 2.0 \times 10^{-6}(T/300)^{-0.7}cm^3$ $molecule^{-1}$ s^{-1}

Recommended branching fractions:
(1a) = 0.04
(1b) = 0.23
(1c) = 0.23
(1d) = 0.22
(1e) = 0.22
(1f) = 0.00

(1g) = 0.06
(1h) = 0.00

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