Author: Wolf Dietrich Geppert (University of Stockholm, Sweden)

$$HCNH^+ + e^- \rightarrow HCN + H \quad (1a)$$
$$\rightarrow HNC + H \quad (1b)$$
$$\rightarrow CN + 2H \quad (1c)$$
$$\rightarrow CN + H_2 \quad (1d)$$

Thermodynamic Data

$\Delta H^o_{298}(1a) \approx -611$ kJ mol^{-1}

$\Delta H^o_{298}(1b) \approx -528$ kJ mol^{-1}

$\Delta H^o_{298}(1c) \approx -76$ kJ mol^{-1}

$\Delta H^o_{298}(1d) \approx -512$ kJ mol^{-1}

Thermochemical data for $HCNH^+$, CN, HCN and HNC were taken from Ref. [1], ΔH^o_{298} of $HCNH^+$, has therein been obtained from the proton affinities of HCN and HNC. All four reactions (1a-d) are enough exoergic to prevent small errors in the thermodynamic data to affect the viability of the process.

Rate Coefficient Data *k*

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
Rate Coefficient Measurements			
$2.8 \times 10^{-7}(T/300)^{-0.65}$	< 1000	[2]	Storage ring
3.5×10^{-7}	300	[3]	Flowing afterglow
Rate Coefficient Reviews and Evaluations			
$2.83 \times 10^{-7}(T/300)^{-0.65}$	10 – 300	UMIST database	
$4.62 \times 10^{-7}(T/300)^{-0.65}$		OSU website	
Branching Fraction Measurements			
1(a+b) = 0.675 ± 0.016		[2]	Storage ring
1(c) = 0.325± 0.017			
1(d) = 0.0 ± 0.017			
H production = 0.63		[3]	Flowing afterglow
Branching Fraction Reviews and Evaluations			
1(a) = 0.34	10 – 300	UMIST database	
1(b) = 0.34			
1(c) = 0.32			
1(a) = 0.4		OSU website	

1(b) = 0.4

1(c) = 0.2

Comments

The overall rate constants measured by the storage ring and flowing afterglow experiments can be regarded a similar, especially in hindsight to the probable error bars of about 20 % prevalent in the CRYRING experiments given the accuracy of the current measure, which was the major source of errors during the time of the experiment. One possible source of errors is the assumption of the authors of the flowing afterglow study that the recombination rate coefficient of H_3^+ is very low (which subsequently has been shown not to be true), but the high velocity of the proton transfer from this ion to HCN probably deprives this fault from having any consequences for the rate constant [4].

The disagreement lies in the branching fraction between the different product channels. In another flowing afterglow study Adams et al. [5] found a branching fraction of hydrogen atoms of 0.63, which would imply a branching fraction of 0.37 – 0.69 for the CN + H_2 for pathway 1(d), dependent on the branching fractions of the other pathways. This channel involves a substantial rearrangement of the intermediate molecule (resulting in a H-migration over two atoms), which seems odd.

Several explanations are possible for the discrepancy of the branching fractions. Firstly, there could be different excitation regimes (ion temperatures) in the ring and afterglow experiments, since cooling is restricted to radiative deactivation and superelastic collisions with electrons in the high vacuum present in storage rings. However, in this case the excited states should have rate constants very similar to the ground state (leading to almost equal rate constants in the two studies), which can be questioned, but not completely ruled out. Secondly there could be different isomers present in the experiments. Two important isomers of H_2CN^+ exist, the linear $HCNH^+$ and the methylenimine cation H_2CN^+. In the storage ring study, the ion was produced through fragmentation of acetonitrile, whereas in the flowing afterglow measurement HCN was protonated by H_3^+ in order to form the desired ion, which could lead to unequal isomer abundances. However, since the H_2CN^+ isomer energetically lies 315 kJ/mol above the $HCNH^+$ one, a substantial presence of H_2CN^+ cannot be expected in either of the studies. Another possibility is the collisional deactivation of excited primary products of the DR in the afterglow experiments (in this case HCN or HNC), which can fragment further (to CN + H) in the ring study. This could lead to a higher branching fraction of reaction 1(c) using the latter method. Such a possibility was recently invoked for explaining the differences in the branching fractions of the dissociative recombination of CH_5^+ [6]. Theoretical studies, however, seem to indicate a concerted mechanism of the 2H + CN production [1]. Also, collisional deactivation cannot explain the large fraction of channel 1(d) in the afterglow experiment.

Another important question is the distribution between HCN and HCN production. Experiments are on the way at the Glosik group in Prague to measure that HCN/HNC product ratio, but so far one has to resort to resort to theoretical calculations. Such computations have been carried out both by Talbi and Ellinger [7] as well as Shiba et al. [8]. Although they disagree on the mechanism of the dissociative recombination of $HCNH^+$, the both conclude that HCN and HNC are produced in equal amounts.

Preferred Values

Recommended rate constant:

$k = 2.83 \times 10^{-7}(T/300)^{-0.65}$ cm^3 molecule^{-1} s^{-1}

Recommended branching fractions:

1(a) = 0.34

1(b) = 0.34

1(c) = 0.32

1(d) = 0.00

Comments on Preferred Values

For the rate constant, the values from the rate constants are in good agreement, so the choice will not affect the models gravely. Since the ring measurement spans a larger energy range, we recommend using the value obtained there.

The error bars of the productions of H atoms in the afterglow experiments amount to 20-30% and the H atom yield is determined indirectly, relying on several calibrations involving different reaction steps and on the exact knowledge of the efficiency and. In the ring experiments the branching fractions

of the three processes 1(a+b), 1(c) and 1(d) were measured using a comparatively simple technique. Therefore one is more inclined to recommend the ring results, although it is definitely too early to close the books.

If one assumes that all the hydrogen in the flowing afterglow experiment stems from reactions 1(a) and 1(b), the agreement for the sum of their branching fractions is very satisfactory (0.63 versus 0,675). The difference then lies in the relative importance of channel 1(c) and 1(d), which from astrochemical viewpoint (production of H_2 instead of 2H) is probably purely academic.

Since there is no measurement of the HCN/HNC production ratio and the theoreticians point to an equal distribution between those channels, there seems to be no reason to question this assumption, which is already made the present models.

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