Authors:

Jean-Christophe Loison (Univ. of Bordeaux - CNRS, Fr)

Dahbia Talbi (Univ. of Montpellier – CNRS, Fr)

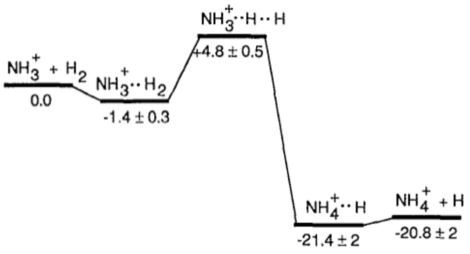
$NH_3^+(X^2A''_2) + H_2(X^1\Sigma_g^+) \rightarrow NH_4^+(X\ ^1A_1) + H(^2S)$ $\Delta Hr^{298} = -87$ kJ mol^{-1} (*)

Rate Coefficient Data *k*

k / cm^3 molecule^{-1} s^{-1}	*T* / K	Reference	Comments
Rate Coefficient Measurements (k)			
5×10^{-13}	300	Kim *et al*, 1975	(2)
$1.7 \times 10^{-11} \times \exp(-1200/T)$	300-800	Fehsenfeld *et al*, 1975	(3)
$(2.09 \pm 0.22) \times 10^{-11}$	85-510	Adams and Smith, 1984	(4)
Complex dependency	20-298	Borhinger, 1985	(5)
$3.36\times10^{-14}\times\exp(35.7/T)$	11-20	Barlow and Dunn, 1987	(6)
Theory			
Complex dependency	5-350	Herbst *et al*, 1991	(1)
Reviews and Evaluation			
$3.36\text{x}10^{-14}\ \exp(35.7/T)$	10-20	UMIST database	
$2.0\text{x}10^{-13}$	20-300	UMIST database	
$1.7\text{x}10^{-11}\ \exp(-1044/T)$	300-41000	UMIST database	
$1.5\text{x}10^{-14}\ (T/300)^{-1.5}$		OSU database	

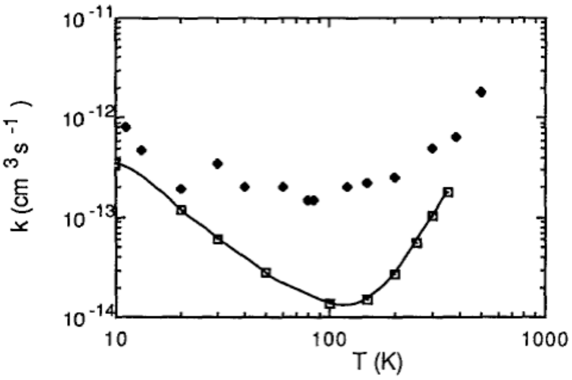
Comments

There have been various experimental investigations of this reaction. Original studies by Kim *et al.* and Fehsenfeld *et al* showed the reaction to be quite slow at room temperature *(k* = 5×10^{-13} cm^3 molecule^{-1} s^{-1}) and to increase in rate with increasing temperature, indicating a system with an activation energy of approximately 2.1 kcal mol^{-1} (8.8 kJ mol^{-1}). Subsequent experimental work by Adams and Smith indicated however that the rate coefficient does not obey a typical Arrhenius relation at temperatures significantly under 300 K but rather levels off at temperatures near 80-100 K. Finally, work by Luine and Dunn and Bohringer showed that the rate coefficient actually increases at still lower temperatures.



from Herbst et al. (1) (unit in kcal mol^{-1})

At low temperatures, the lifetime of the complex is quite long and even a small tunneling probability can be important. Barlow and Dunn extended the work of Luine and Dunn and studied the effects of deuterium substitution on the rate of the reaction at low temperature. Their results strongly support the tunneling hypothesis.



Experimental rate coefficients (filled diamonds) and calculated one (open square). from Herbst et al. (1)

The rate coefficients calculated using a phase space theory approach (1) where the formation of an initial complex is considered, and from which tunneling under a small transition state barrier could occur are lower than the measured values, even when large uncertainties are considered for the calculated barrier height and imaginary vibrational frequency. The lower calculated value for the rate coefficient may be due either to the fact that in the experimental determination, part of the reaction is due to three-body mechanism or to the fact that the rate of tunneling have been calculated using an Eckart potential, which may lead to substantial error as the tunneling is notoriously sensitive to details of the potential surface such as the height and imaginary vibrational frequency which regulate the steepness of the barrier.

Preferred Values

Rate coefficient (10 – 20 K)

k (T) = $3.36\times10^{-14}\times\exp(35.7/T)$ cm^3 molecule^{-1} s^{-1}

Rate coefficient (20 – 230 K)

k (T) = 2.0×10^{-13} cm^3 molecule^{-1} s^{-1}

Rate coefficient (230 – 800 K)

k (T) = $1.7\times10^{-11}\times\exp(-1044/T)$ cm^3 molecule^{-1} s^{-1}

Reliability

$F_0 = 1.5$, $g = 0$

Comments on Preferred Values

There are some uncertainties at low temperature if the three-body mechanism plays an important role.

References

(*) D. L. Baulch *et al.*, J. Phys. Chem. Ref. Data **34**, 575 (2005).
(1) E Herbst, DJ DeFrees, D Talbi, F Pauzat, W Koch, AD McLean: J. Chem. Phys. 94 (1991) 7842-49.
(2) JK Kim, LP Beard, WT Huntress Jr: J. Chem. Phys. 62 (1975) 45-52.
(3) FC Fehsenfeld, W Lindinger, AL Schmeltekopf, DL Albritton, EE Ferguson: J. Chem. Phys. 62 (1975) 2001-03.
(4) NG Adams, D Smith: Int. J. Mass Spectrom. Ion Proc. 61 (1984) 133.
(5) H Bohringer: Chem. Phys. Lett. 122 (1985) 185
(6) SE Barlow, GH Dunn: Int. J. Mass Spectrom. Ion Proc. 80 (1987) 227