Authors:

Ian Smith (University of Cambridge, UK)

Jean-Christophe Loison, Astrid Bergeat (Université de Bordeaux, France)

Eric Herbst (The Ohio State University, USA)

$$C_2H_2^+ + H_2(^1\Sigma^+_g) \rightarrow C_2H_4^+ \qquad (1)$$

Thermodynamic Data

$\Delta H^o_{298}(1) = -260$ kJ mol^{-1}

$\Delta_f H^o_{298}(C_2H_2^+) = 1326.7$ kJ mol^{-1} (1), $\Delta_f H^o_{298}(C_2H_4^+) = 1066.9$ kJ mol^{-1} (1)

Rate Coefficient Data *k*

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
7×10^{-14} (*n*-H_2)	80	(2)	
1.3×10^{-12} (*n*-H_2)	10	(3,4)	
4.7×10^{-12} (*p*-H_2)	10	(3,4)	
Calculations:			
4.3×10^{-14} (T/300)$^{-1.0}$ (*e*-H_2)	2-80	(5)	without tunnelling
2.3×10^{-15} (T/300)$^{-1.5}$(*e*-H_2)	2-80	(5)	with tunnelling
Evaluations			
2.34×10^{-14} (T/300)$^{-1.5}$	10 – 300	udfa (UMIST database)	
1.5×10^{-14} (T/300)$^{-1.0}$		OSU website	

p-H_2 = para H_2, *n*-H_2 = normal H_2 = fixed ratio *o*-H_2/ *p*-H_2 = 3.1 (equal to the ratio at ambient temperature), *e*-H_2= equilibrium H_2 at a given temperature so 99.9999% of *p*-H_2 at 10K (99.0% of *p*-H_2 at 25K and 51.4% of *p*-H_2 at 80K).

Comments

The review by Gerlich and Horning (2) reports the results of experiments at 80 K in a ring-electrode ion trap. The later experiments reported by Gerlich (3,4) were performed in a 22-pole ion trap. If both results are correct, they indicate a strong *T*-dependence below about 80 K, as assumed in the UMIST database. In ref. (3,4), Gerlich experimentally examines and carefully discusses the possibility of a bimolecular reaction to $C_2H_3^+$ + H (as suggested by Hawley and Mark Smith). The experiments provided strong evidence that any contribution from the bimolecular channel to the overall rate coefficient was eliminated – at least, at 10 K.

Little is known about the *T*-dependence of this reaction. Interpretation is complicated by the possible influence of the slightly endothermic reaction to $C_2H_3^+$ + H. *Ab-initio* calculations (5) suggest that there is a small entrance channel barrier under which low-temperature reactants must tunnel to access the deep potential well associated with $C_2H_4^+$. In the same article, the authors have calculated using phase space theory the radiative association rate constant including tunneling for both the formation and redissociation of the $C_2H_4^+$ complex. However, this calculation with tunneling does not reproduce low-temperature experimental measurements of the rate of the association channel. Rather, a phase space calculation in which it is assumed that the entrance channel barrier does not exist is in better agreement with most of the experimental data, even if there is still a notable underestimation at low temperature (1.3×10^{-12} instead of 4.7×10^{-12} at 10 K for *e*-H_2 which is only *p*-H_2 at 10K, the agreement being better at 80 K: 8.6×10^{-14} for *n*-H_2 instead of 7×10^{-14}). The T dependence is found to be T^{-1} using the rate constant without tunneling and $T^{-1.5}$ using the rate constant with tunneling. It is not obvious how to determine the accuracy of the theoretical T dependence because, if the tunneling is not well described, it strongly affects this dependence. Moreover the experimental rate constants at 10 K and 80 K lead to a $T^{-1.5}$ dependence, and it seem reasonable to choose this value, although the exponent should decrease as the H_2 rotation freezes out at low temperatures (6).

Preferred Values

$k_{RA}(10\ \mathrm{K}) = 4.7 \times 10^{-12}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$

$k_{RA}\ (T, p\text{-}H_2) = 2.9 \times 10^{-14} (T/298)^{-1.5}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$
$k_{RA}\ (T, o\text{-}H_2) = 6.3 \times 10^{-15} (T/298)^{-1.5}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$

$F_0 = 3$; $g = 0$

k varies between k(T)/F and k(T)*F
g defined by $F(T)=F_0 *\exp(g(1/T-1/300))$

With J. Phys. Chem. Ref. Data standard:
$F_{298} = 10^{\Delta\log(k)}$ and $g = \sigma(E^{\#})$ if $\Delta\log(k)$ and $\sigma(E^{\#})$ refer to 1σ.

Comments on Preferred Values

At 10 K, the recommended rate coefficient assumes that H_2 is in the *para*-form in dense ISCs. It is essentially the same as in the UMIST and OSU databases. An uncertainty of a factor of three is suggested. Again, there is uncertainty associated with not knowing the *ortho*-H_2 to *para*-H_2 ratio in the ISM and whether the distribution of the ions over its internal states is the same in the experiments and the ISM.

References

(1) DL Baulch, CT Bowman, CJ Cobos, RA Cox, T Just, JA Kerr, MJ Pilling, D Stocker, J Troe, W Tsang, RW Walker, J Warnatz: J. Phys. Chem. Ref. Data 34 (2005) 757-1397.

(2) D Gerlich, S Horning: Chem. Rev. 92 (1992) 1509.

(3) D Gerlich: Physica Scripta T59 (1995) 256.

(4) D Gerlich, Molecules and Grains in Space. AIP Press, New York, 1994.

(5) E Herbst, K Yamashita: J. Chem. Soc., Faraday Trans 89 (1993) 2175-83.

(6) D R Bates and E Herbst: Rate Coefficients in Astrochemistry, ed. T J Millar, D.A. Williams. Kluwer, Dordrecht, 1988