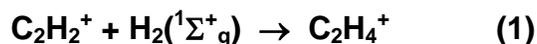


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Thermodynamic Data

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

$$\Delta_f H^{\circ}_{298}(\text{C}_2\text{H}_2^+) = 1326.7 \text{ kJ mol}^{-1} (1), \Delta_f H^{\circ}_{298}(\text{C}_2\text{H}_4^+) = 1066.9 \text{ kJ mol}^{-1} (1)$$

Rate Coefficient Data k

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T / K	Reference	Comments
7×10^{-14} ($n\text{-H}_2$)	80	(2)	
1.3×10^{-12} ($n\text{-H}_2$)	10	(3,4)	
4.7×10^{-12} ($p\text{-H}_2$)	10	(3,4)	
<i>Calculations:</i>			
$4.3 \times 10^{-14} (\text{T}/300)^{-1.0}$ ($e\text{-H}_2$)	2-80	(5)	without tunnelling
$2.3 \times 10^{-15} (\text{T}/300)^{-1.5}$ ($e\text{-H}_2$)	2-80	(5)	with tunnelling
<i>Evaluations</i>			
$2.34 \times 10^{-14} (\text{T}/300)^{-1.5}$	10 – 300	udfa (UMIST database)	
$1.5 \times 10^{-14} (\text{T}/300)^{-1.0}$		OSU website	

$p\text{-H}_2$ = para H_2 , $n\text{-H}_2$ = normal H_2 = fixed ratio $o\text{-H}_2/p\text{-H}_2 = 3.1$ (equal to the ratio at ambient temperature), $e\text{-H}_2$ = equilibrium H_2 at a given temperature so 99.9999% of $p\text{-H}_2$ at 10K (99.0% of $p\text{-H}_2$ at 25K and 51.4% of $p\text{-H}_2$ 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 -H₂ which is only p -H₂ at 10K, the agreement being better at 80 K: 8.6×10^{-14} for n -H₂ 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 H₂ rotation freezes out at low temperatures (6).

Preferred Values

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

$$k_{RA}(T, p\text{-H}_2) = 2.9 \times 10^{-14} (T/298)^{-1.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
$$k_{RA}(T, o\text{-H}_2) = 6.3 \times 10^{-15} (T/298)^{-1.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$F_0 = 3 ; g = 0$$

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 H₂ 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*-H₂ to *para*-H₂ 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

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