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$CH_3^+ + H_2(^1\Sigma^+) \rightarrow CH_5^+$ (1)

Thermodynamic Data

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

$\Delta_f H^o_{298}(CH_3^+) = 1095$ kJ mol^{-1} [1]

$\Delta_f H^o_{298}() =$ kJ mol^{-1} [1]

Rate Coefficient Data *k*

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
1.1×10^{-13}	11		(a) measured in Penning ion trap; cited in (b)
6×10^{-15}	80		(c) measured in ring-electrode ion trap apparatus, cited in (b).
$(5.0 \pm 2.0) \times 10^{-14}$ (n-H_2)	10		measured in 22-pole rf trap and reported by Gerlich in (d)
$(1.1 \pm 0.1) \times 10^{-13}$ (p-H_2)	10		
Evaluations			
1.3×10^{-14} (T/300)$^{-1.0}$	10 – 300	udfa (UMIST database)	
1.3×10^{-14} (T/300)$^{-1.0}$		OSU website	

Comments

The review by Gerlich and Horning (b) provides information about the studies of the three-body collisional process. They appear to be in quite good agreement and indicate relatively little T-dependence below about 80 K. Smith's calculations (e) gave quite good agreement with the SIFT data (down to 80 K). If k_{RA} is estimated from the collisional rate constant using an estimated value of k_{rad} for IR radiative transitions, the result is fairly close to the 80 K experimental value but significantly below the 13 K value of Dunn and co-workers. It has been proposed that electronic transitions play a role – but this hypothesis is rejected by Bacchus-Montabonel *et al.* (f) on the basis of their *ab initio* calculations. The values recommended in the UMIST and Ohio data bases seem to give strong weight to the Dunn data.

The later *ab initio* theoretical calculations carried out by Talbi and co-workers (e) – based on stabilisation by IR transitions - give a rate constant at 80 K quite close to the experimental value (c), especially bearing in mind the wide error limits on the latter. However, the calculated value at 10 K is two orders-of-magnitude lower than the value reported at 13 K by Dunn and co-workers.

The later – and latest – data from Gerlich's laboratory (d) are in good agreement with the earlier data of Dunn and co-workers. Therefore it seems possible to recommend this low temperature value with some confidence. However, in transferring these data to interstellar conditions, there is uncertainty in respect of both the *ortho-para* ratio and nuclear spin effects on the reaction rate. In addition, the internal state distributions may not be the same in the experiments and in the interstellar medium.

Smith and Adams (c) have studied the three-body reaction $CH_3^+ + H_2 + He$ at 82, 200, 287 and 520 K. The rate coefficients fit the function 9.1×10^{-29} $(T/298)^{-2.3}$ cm^6 molecule^{-2} s^{-1}. If it is assumed that collisional stabilisation and radiative association have similar T-dependences, which is expected if the rate coefficients for both radiative emission and collisional stabilisation are independent ot temperature (g), one can obtain a T-dependence for k_{RA} by assuming (i) the form: $k_{RA}(T) = \alpha(T/298)^{\beta}\exp(-\gamma/T)$; (ii) that $\beta = -2.3$ (from the measurements on the 3-body association); (iii) that values of α and γ are determined by the values of k_{RA}(10 K) and k_{RA}(80 K), measured by Gerlich and co-workers. Then for the reaction of n-H_2:

$$k_{RA}(T) = 4.1 \times 10^{-16}(T/298)^{-2.3}\exp(-30/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Preferred Values

k(298 K) = 3.7×10^{-16} cm^3 molecule^{-1} s^{-1}

for p-H_2 :

k(10 K) = 1.1×10^{-13} cm^3 molecule^{-1} s^{-1}

$$k(T) = 3.78 \times 10^{-16}(T/298)^{-2.3}\exp(-21.5/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

for n-H_2 :

k(10 K) = 5.0×10^{-14} cm^3 molecule^{-1} s^{-1}

$$k_{RA}(T) = 4.1 \times 10^{-16}(T/298)^{-2.3}\exp(-30/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$F_0 = 3$ - $g = 0$

Comments on Preferred Values

The recommended value at 10 K is that given by both Dunn and co-workers (a) and Gerlich (d). Some uncertainty arises from questions about the state of H_2 (*normal* or *para-*) in dense ISCs. I suggest a factor of 3 uncertainty overall at 10 K; that is, $\Delta log\ k = 0.5$. The recommended value at 10 K is essentially that in the OSU and UMIST databases.

References

(a) S. E. Barlow, G. H. Dunn and M. Schauer, *Phys. Rev. Lett.*, **52**, 902 (1984); Barlow, S. E.; Dunn, G. H.; Schauer, K. *Phys. Rev. Lett.*, **53**, *Phys. Rev. Lett.* 1984, **53**, 1610 (1984).

(b) D. Gerlich and S. Hornig, *Chem. Rev.*, **92**, 1509 (1992).

(c) D. Gerlich and G. Kaefer,.*Astrophys. J.* **347**, 849 (1989).

(d) D. Gerlich, *Physica Scripta*, **T59**, 256 (1995);
D. Gerlich in *Molecules and Grains in Space* (ed. I. Nenner, AIP Press, New York, 1994)

(e) I. W. M. Smith, *Astrophys. J.*, **347**, 282 (1989).

(f) D. Talbi and M. C. Bacchus-Montabonel, *Chem. Phys.*, **232**, 267 (1998); M. C. Bacchus-Montabonel, D. Talbi and M. Persico, *J. Phys. B,* **33**, 955 (2000).

(g) The rate constant for collisional stabilisation will be independent of temperature if Langevin theory holds.