Author: Ian Smith (University of Cambridge, UK)

$$C^+(^2P) + H_2(^1\Sigma^+) \rightarrow CH_2^+ \qquad (1)$$

Thermodynamic Data

$\Delta H^o_{298}(1) = -433$ kJ mol^{-1}

$\Delta_f H^o_{298}(C^+(^2P)) = 1803$ kJ mol^{-1} [1]

$\Delta_f H^o_{298}(CH_2^+) = 1370$ kJ mol^{-1} [1]

Rate Coefficient Data *k*

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
$k(C^+(^2P) + p\text{-}H_2) = 1.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 10 K		(a), (b)	
$k(C^+(^2P) + n\text{-}H_2) = 6.8 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 10 K		(a), (b)	
Evaluations			
4×10^{-16} (T/300)$^{-0.2}$	10 – 300	udfa (UMIST database)	
4×10^{-16} (T/300)$^{-0.2}$		OSU website	

Comments

Gerlich and co-workers (a, b) have studied the reaction of C^+ with both *para*-H_2 and *normal*-H_2 at 10 K over a wide range of H_2 densities, thereby observing both the three-body reaction and the radiative association.

Smith (c) has carried out calculations on the radiative association reaction. Assuming stabilisation only by IR emission on the ground state PES yielded rate coefficients much lower than those determined experimentally (and similar to those for C + H_2, where only IR transitions are allowed). However, besides the $^2A_1$ electronic ground state, an excited $^2B_1$ state is accessible. Assuming $k_{rad} = 10^5$ s^{-1}, Smith obtained remarkable (and fortuitous) agreement with the rate coefficients reported (later) by Gerlich. Earlier calculations by Herbst (d) which recognised the mixing of levels from the $^2A_1$ and $^2B_1$ states suggested a value of k_{RA} between 10^{-15} and 10^{-16} cm^3 s^{-1}.

Smith and Adams (e) have studied the three-body reaction $C^+ + H_2 + He$ at 82, 200 and 287 K. The rate coefficients at these temperatures fit the function 8.8×10^{-30} $(T/298)^{-1.3}$ cm^6 molecule^{-2} s^{-1}.

The T-dependence of the association reaction is discussed by Gerlich and Horning (f). They suggest that the rate coefficients k_{RA} level off below *ca.* 40 K.

To obtain a T-dependence for k_{RA} I have assumed (i) the form: $k_{RA}(T) = \alpha(T/298)^{\beta}\exp(\gamma/T)$; (ii) that $\beta = -1.3$ (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.

Preferred Values

$k_{RA}(298\text{ K}) = 1.8 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}
for p-H_2
$k_{RA}(10\text{ K}) = 1.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}
$k_{RA}(T) = 2.0 \times 10^{-16}(T/298)^{-1.3}\exp(-23/T)$
cm^3 molecule^{-1} s^{-1}

$F_0 = 3$; $g = 0$

Comments on Preferred Values

Input is needed on the form of H_2 in ISCs. Here, it is assumed that it exists as p-H_2; that is, in $J = 0$. The expressions in the UMIST and OSU data bases yield $k(10\text{ K}) = 7.9 \times 10^{-16}$ cm^3 molecule^{-1}

s^{-1}. It seems reasonable to assume that $\Delta log\ k_{RA} = 0.5$ to include both the uncertainty in the form of H_2 and experimental error.

References

(a) D. Gerlich in *Molecules and Grains in Space* (ed. I. Nenner, AIP Press, New York, 1994)
(b) D. Gerlich in *Low Temperatures and Cold Molecules* (ed. I. W. M. Smith, World Scientific, 2008)
(c) I. W. M. Smith, *Astrophys. J.*, **347**, 282 (1989).
(d) E. Herbst, *Astrophys. J.*, **252**, 810 (1982).
(e) N. G. Adams and D. Smith, *Chem. Phys. Lett.*, **79**, 563 (1981)
(f) D. Gerlich and S. Horning, *Chem. Rev.*, **92**, 1509 (1992)