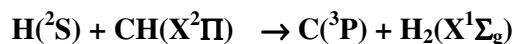


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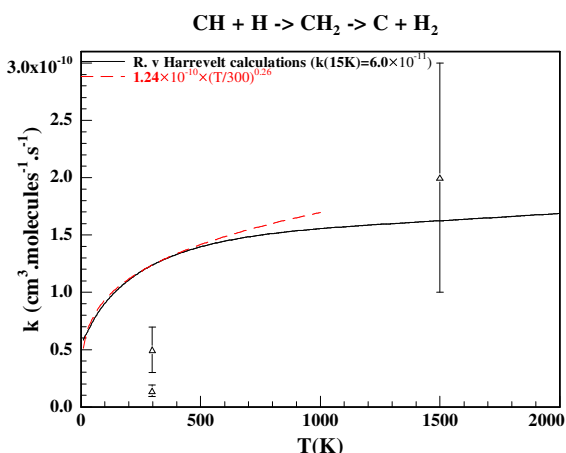
Thermodynamic Data

$$\Delta H_{298}^{\circ} = -97.7 \text{ kJ mol}^{-1} \quad (1)$$

Rate Coefficient Data k

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T / K	Reference	Ref
<i>Rate Coefficient Measurements</i>			
$k = 4.98 \times 10^{-11}$	298	Grebe and Homann 1982	(2)
$k = 1.4 \times 10^{-11}$	297	Becker <i>et al.</i> , 1989	(3)
$k = 2.0 \times 10^{-10}$	1500-2500	Dean <i>et al.</i> , 1991	(4)
<i>Theory</i>			
$k = 1.24 \times 10^{-10} \times (T/300)^{0.26}$	50-500K	Rob van Harrevelt <i>et al.</i> , 2002	(5)

Comments



The reactants correlate with two singlet and two triplet surfaces $^{1,3}(A'+A'')$ and products with three triplet surfaces $^3(2A'+A'')$. Moreover ab-initio calculations (5) show no barrier for CH₂ formation only for $^3A''$, $^1A'$ and $^1A''$ surfaces. There is then a 3/8 electronic degeneracy factor. Quasiclassical calculations (5) show that most collisions ($\approx 80\%$) are nonreactive, because of a too-weak excitation of the CH vibration after a H-CH collision with H approaching CH with HCH angles larger than 60 deg leading to a smaller value than capture rate theory.

There are few scattered measurements for this reaction. Two are direct measurements of the

global rate coefficient near 300 K and one is an indirect measurement, a priori less reliable, at higher temperature. There are also various theoretical studies, the latest one by Rob van Harrevelt *et al* (5) being very complete. Their calculated rate constant is in agreement with the indirect measurement by Dean *et al* (4) but not with the, a priori, more precise direct measurement by Becker *et al* (3). Becker *et al.* used micro wave dissociation to produce H atoms from H₂ molecules and determine H atoms concentrations with the H + NO₂ reaction. As CH radical reacts with the H₂ molecule, this is a quite delicate system. We propose a preferred value issue from the calculated values with a uniform error distribution to take in account the experimental data.

Preferred Values

$$k(T) = 1.24 \times 10^{-10} \times (T/300)^{0.26} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Reliability

$$F(10-500\text{K}) = 3 \quad (g=14)$$

(g defined by $F(T) = F(298) \times \exp(-g(1/T - 1/298))$) with uniform distribution (constant probability to found k between $6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)

The theoretical calculations have been performed only down to 50 K in the article but have been performed down to 10 K by the authors for this datasheet (personal communication)

Comments on Preferred Values

As there are few measurements, the reliability of this rate constant is quite low.

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) J Grebe, K Homann: *Ber. Bunsenges. Phys. Chem.* 86 (1982) 587.
- (3) KH Becker, B Engelhardt, P Wiesen, KD Bayes: *Chemical Physics Letters* 154 (1989) 342-48.
- (4) AJ Dean, DF Davidson, RK Hanson: *The Journal of Physical Chemistry* 95 (1991) 183-91.
- (5) R van Harrevelt, MC van Hemert, GC Schatz: *The Journal of Chemical Physics* 116 (2002) 6002-11.