

Evaluation of rate data

Examination of available rate data from the literature and recommendation of rate parameters over specified temperature range, together with uncertainties.

Evaluated Kinetic Data for Combustion Modeling: Supplement II

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The next few slides show the structure of a typical data sheet



1. Thermodynamic Data

$$\Delta H^\circ_{298} = -68.29 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{298} = -25.04 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$K_c = 3.48 \cdot 10^{-3} T^{0.367} \exp(+8390/T)$$

$(300 \leq T/\text{K} \leq 5000)$

2. Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$2.0 \cdot 10^{-11} \exp(112/T)$	221–499	Lewis and Watson, 1980 ¹	(a)
$3.8 \cdot 10^{-11}$	298	Howard and Smith, 1980 ²	(b)
$6.7 \cdot 10^{-10} T^{-0.5}$	250–515	Howard and Smith, 1981 ³	(b)
$3.1 \cdot 10^{-11}$	300	Brune, Schwab, and Anderson, 1983 ⁴	(c)
$3.5 \cdot 10^{-11}$	299	Keyser, 1983 ⁵	(d)
$4.2 \cdot 10^{-11}$	294	Smith and Stewart, 1994 ⁶	(e)
$4.5 \cdot 10^{-11}$	227		
$5.2 \cdot 10^{-11}$	190		
$6.1 \cdot 10^{-11}$	158		
<i>Review and Evaluations</i>			
$5.42 \cdot 10^{-13} T^{0.335} \exp(1112/T)$	1000–3300	Michael, 1992 ⁷	(f)
$2.0 \cdot 10^{-11} \exp(112/T)$	220–500	CRC, 1992; 1994 ⁸	(g)
$2.4 \cdot 10^{-11}$	1000–2000		
$2.2 \cdot 10^{-11} \exp(120/T)$	220–500	NASA, 1997 ⁹	(h)
$2.3 \cdot 10^{-11} \exp(110/T)$	220–500	IUBAC, 1997 ¹⁰	(i)

Provides data on recent measurements and evaluations, including
 Rate coefficient
 T/K
 Reference
 Link to comments

Comments (examples)

- (e) Fast flow system in which OH radicals were created by pulsed laser photolysis at 266 nm of HNO₃ in the presence of a much higher concentration of O atoms previously produced upstream of the HNO₃ injection point by the N+NO reaction. [OH] was monitored by LIF, pumping at ~ 282.5 nm and observing at ~ 310 nm. The time delay between the pulse generating OH and the LIF probe pulse was varied. Results were also obtained at 103 K, 50 K, and 10 K but with large uncertainties.
- (f) Calculated from thermodynamic data and $k(\text{H}+\text{O}_2)$.
- (g) Expression of Lewis and Watson¹ adopted for low temperature range and high temperature expression derived from thermodynamic data and $k(\text{H}+\text{O}_2)$.

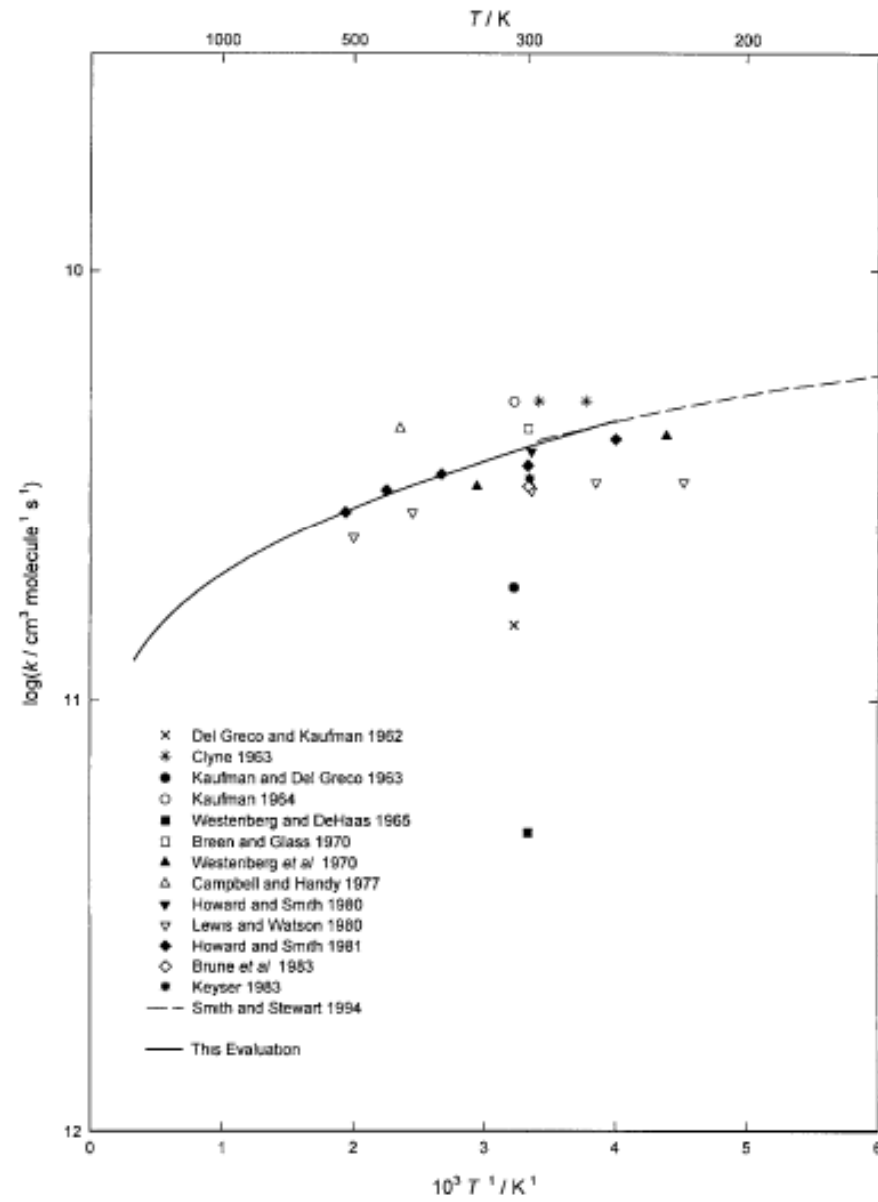
Preferred values

- $k = 2.00 \cdot 10^{-10} T^{-0.352} \exp(113/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
over the range 250-3000 K.
- *Reliability*
- $\Delta \log k = \pm 0.2$ over the range 250-3000 K.

Comments on preferred values

- The only direct studies on this reaction have been carried out at low temperatures where there is excellent agreement among the more recent of them.
- Although there have been no direct measurements of k above 515 K the reverse reaction has been extensively investigated at temperatures in the range 800-3400 K. The preferred expression for k has been derived, therefore, by a fit to the data obtained by combining the expression for $k(\text{H}+\text{O}_2)$ from the present evaluation with the thermodynamic data at temperatures above 800 K together with the directly obtained experimental data at temperatures below 500 K. The reaction has been the subject of a number of theoretical studies; see Miller,¹⁹⁻²¹ Troe,²² Harding *et al.*²³ and Troe and Ushakov.²⁴

Arrhenius Plot



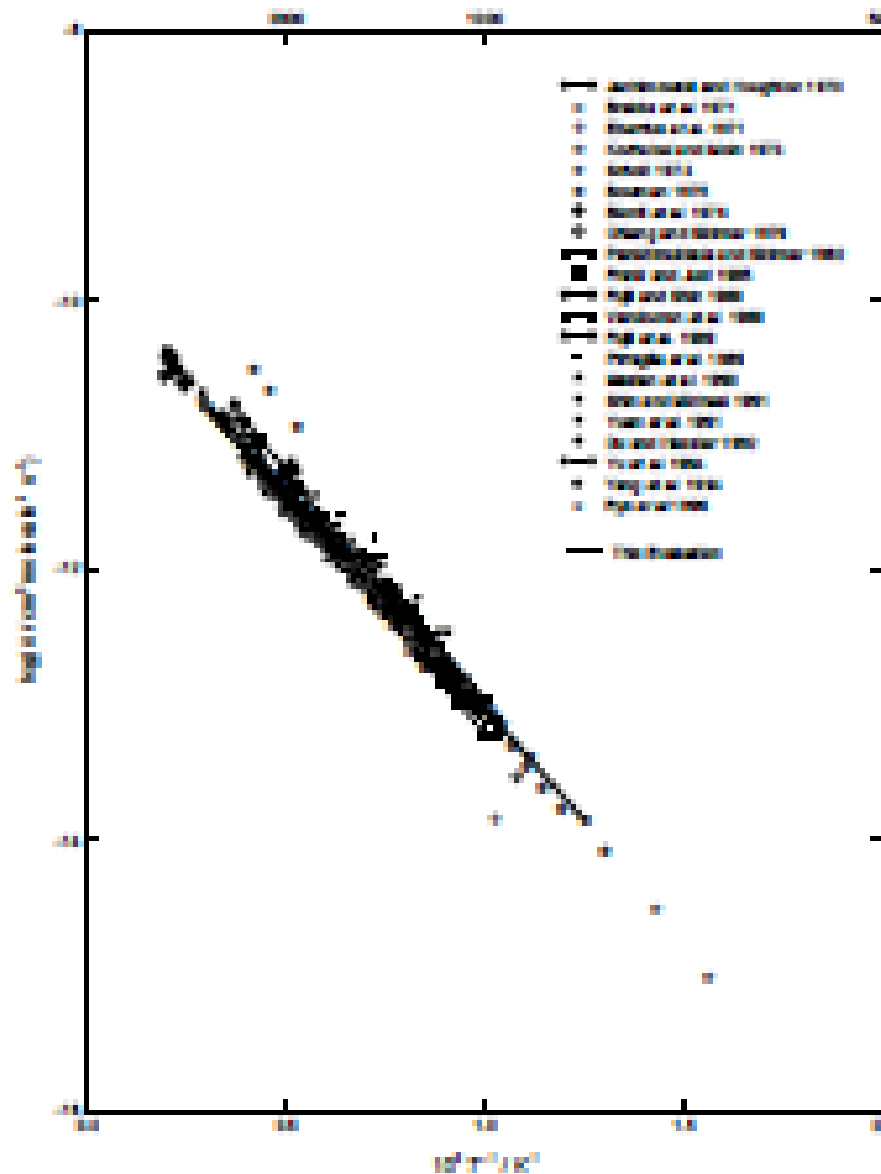
Reverse reaction: $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$

- $k = 3.43 \cdot 10^{-10} T^{-0.097} \exp(-7560/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 800-3500 K.
- $\Delta \log k = \pm 0.1$ at 800 K, rising to ± 0.2 at 3500 K.
- There are no direct measurements of k below 500 K and the recommended values are based on data obtained at temperatures above 800 K. The majority of the determinations of k have been made using shock tube techniques and, generally, are in good agreement.^{1-10,15-25} There is a trend in the more recent studies¹⁻¹⁰ to give slightly lower values of E/R than most of the older determinations.^{11,5-25} Our preferred expression for k is based on the more recent studies, which are cited in the Table. The expression derived gives values very similar to the expression used by Smith *et al.*²⁶ in modelling studies using the GRI mechanism.



Figure is too small to read but it shows the large number of Investigations and demonstrates how the results mainly cluster around the best fit line.

Illustrates the ideas of upper and lower bounds and of a probability distribution function (pdf)



$^3\text{CH}_2 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}$ - an example with limited measurements

Rate Coefficient Data

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T / K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$5 \cdot 10^{-11}$	298	Pilling and Robertson, 1975 ¹	(a)
$1.0 \cdot 10^{-10}$	298	Laufer and Bass, 1975 ²	(b)
$3 \cdot 10^{-11}$	1800-2700	Olson and Gardiner, 1978 ³	(c)
$3 \cdot 10^{-11}$	1700-2200	Bhaskaran <i>et al.</i> , 1979 ⁴	(d)
$(7-10) \cdot 10^{-11}$	1320-2300	Frank and Braun-Unkhoff, 1987 ⁵	(e)
$1.1 \cdot 10^{-10}$	298	Deters <i>et al.</i> , 1998 ⁶	(f)
$1.7 \cdot 10^{-11}$	1350-2400	Hidaka <i>et al.</i> , 2000 ⁷	(g)
$2.1 \cdot 10^{-10}$	298	Wang and Fockenberg, 2001 ⁸	(h)

7×10^{-11} , when most recent value for $k(\text{CH}_3 + \text{CH}_3)$ used

Shock tube measurements used mechanisms with several steps and literature rate data
 Not possible to correct for more recent values – emphasises need to store raw data to allow accurate re-evaluation

$^3\text{CH}_2 + \text{CH}_3$ continued

- $k = 1.2 \cdot 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 298-3000 K.
- $\Delta \log k = \pm 0.3$ at 298 K, rising to ± 0.7 at 3000 K.

Comments:

- Considerable scatter on the data at 298 K. The rate data of references 1 and 2, which were derived from very similar studies, need correction for the value of the rate constant for the methyl radical recombination used in the simulations.
- Reaction presumed to proceed via an ethyl radical adduct. A significant temperature dependence for k is therefore not expected, - supported by results from the shock tube studies. May suggest a very small negative temperature dependence, but scatter at high T large and, provisionally, a temperature independent k is recommended with substantial error limits.

Pressure dependent reactions - reminder

$$k = \frac{k_0 k_\infty [M]}{k_0 [M] + k_\infty} F = k_0 [M] \left(\frac{1}{1 + k_0 [M] / k_\infty} \right) F$$
$$= k_\infty \left(\frac{k_0 [M] / k_\infty}{1 + k_0 [M] / k_\infty} \right) F.$$

$$\log F \cong \frac{\log F_c}{1 + \left[\frac{\log(k_0 [M] / k_\infty)}{N} \right]^2}, \quad N = 0.75 - 1.27 \log F_c$$

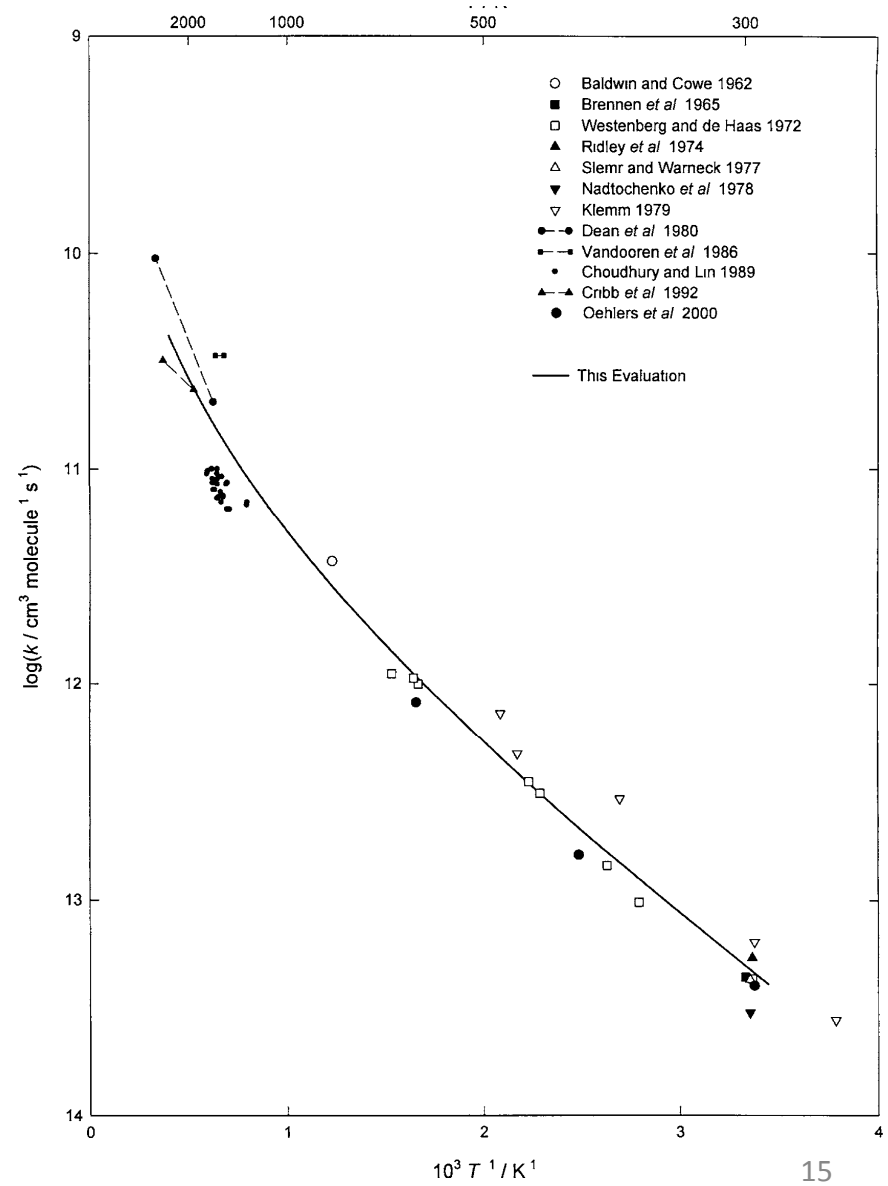
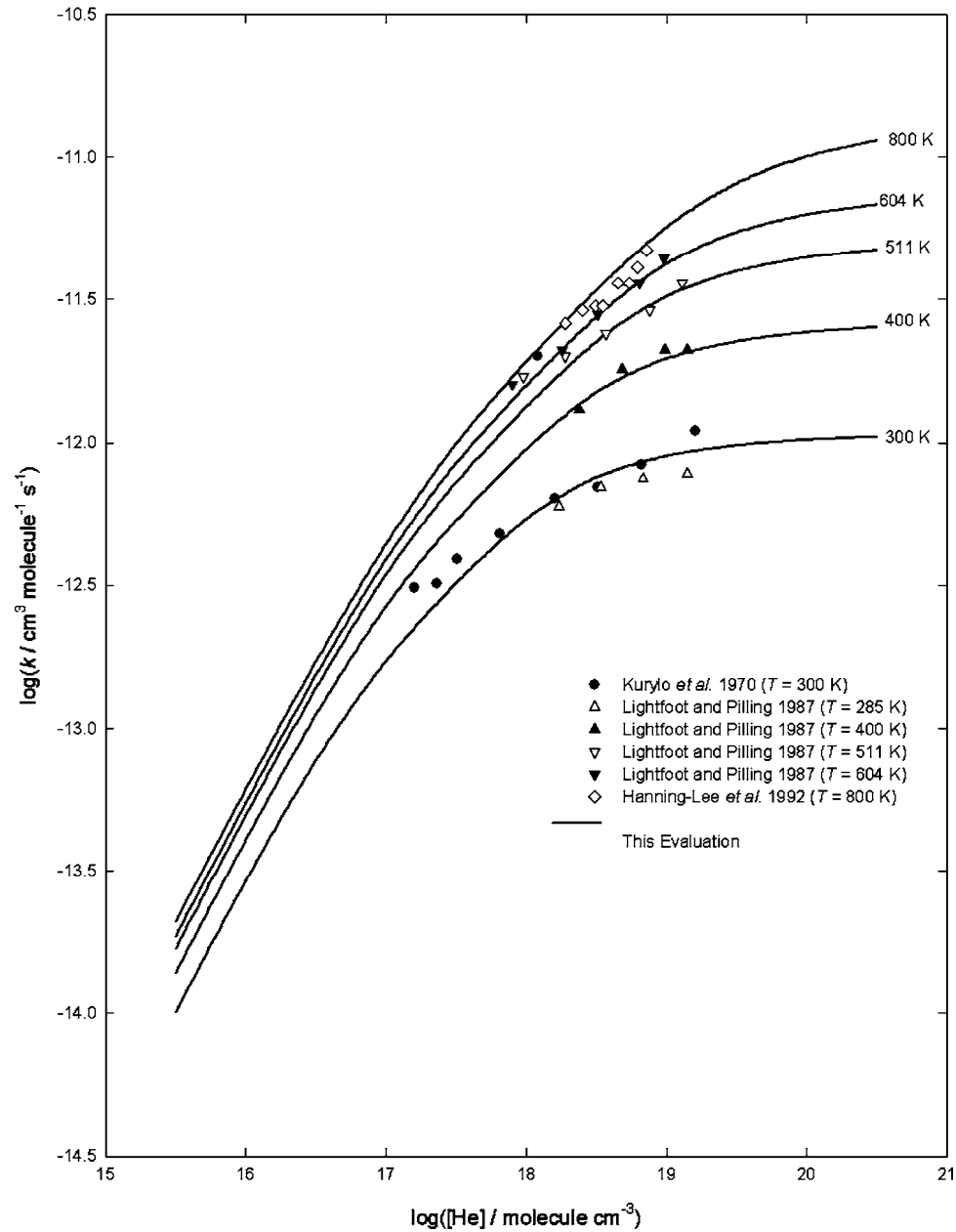
$$F_c = (1 - a) \exp(-T/T^{***}) + a \exp(-T/T^*)$$
$$+ \exp(-T^{**}/T),$$

Pressure dependent reaction: $\text{H} + \text{C}_2\text{H}_4$

- $k_0 = 1.3 \cdot 10^{-29} \exp(-380/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ for $M = \text{He}$ over the range 300-800 K.
- $k_0 = 1.3 \cdot 10^{-29} \exp(-380/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ for $M = \text{N}_2$ over the range 300-800 K.
- $k_\infty = 6.6 \cdot 10^{-15} T^{1.28} \exp(-650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 200-1100 K.
- $F_c = 0.24 \exp(-T/40) + 0.76 \exp(-T/1025)$ for $M = \text{He}$ and N_2 over the range 300-800 K.

Reliability

- $\Delta \log k_0 = \pm 0.3$ for $M = \text{He}, \text{N}_2$ over the range 300-800 K.
- $\Delta \log k_\infty = \pm 0.3$ over the range 200-1100 K.
- $\Delta F_c = \pm 0.1$ for $M = \text{He}, \text{N}_2$ over the range 300-800 K.





Preferred Values

$k_0 = 1.7 \cdot 10^{-6} \exp(-16800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for $\text{M} = \text{C}_2\text{H}_6$ over the range 700–900 K.

$k_\infty = 8.2 \cdot 10^{13} \exp(-20070/T) \text{ s}^{-1}$ over the range 700–1100 K.

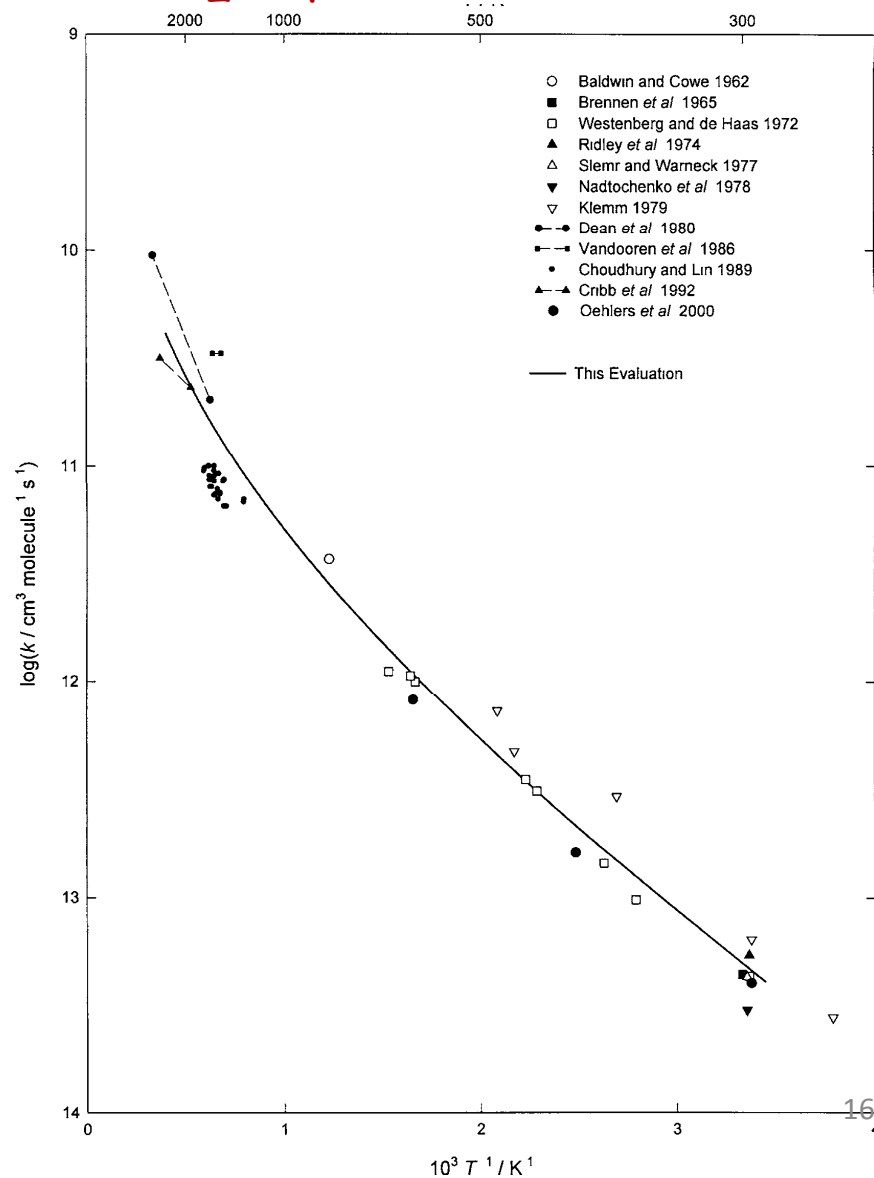
$F_c = 0.25 \exp(-T/97) + 0.75 \exp(-T/1379)$ for $\text{M} = \text{C}_2\text{H}_6$ over the range 700–1100 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ for $\text{M} = \text{C}_2\text{H}_6$ over the range 700–900 K.

$\Delta \log k_\infty = \pm 0.3$ over the range 700–1100 K.

$\Delta F_c = \pm 0.1$ for $\text{M} = \text{C}_2\text{H}_6$ over the range 700–1100 K.



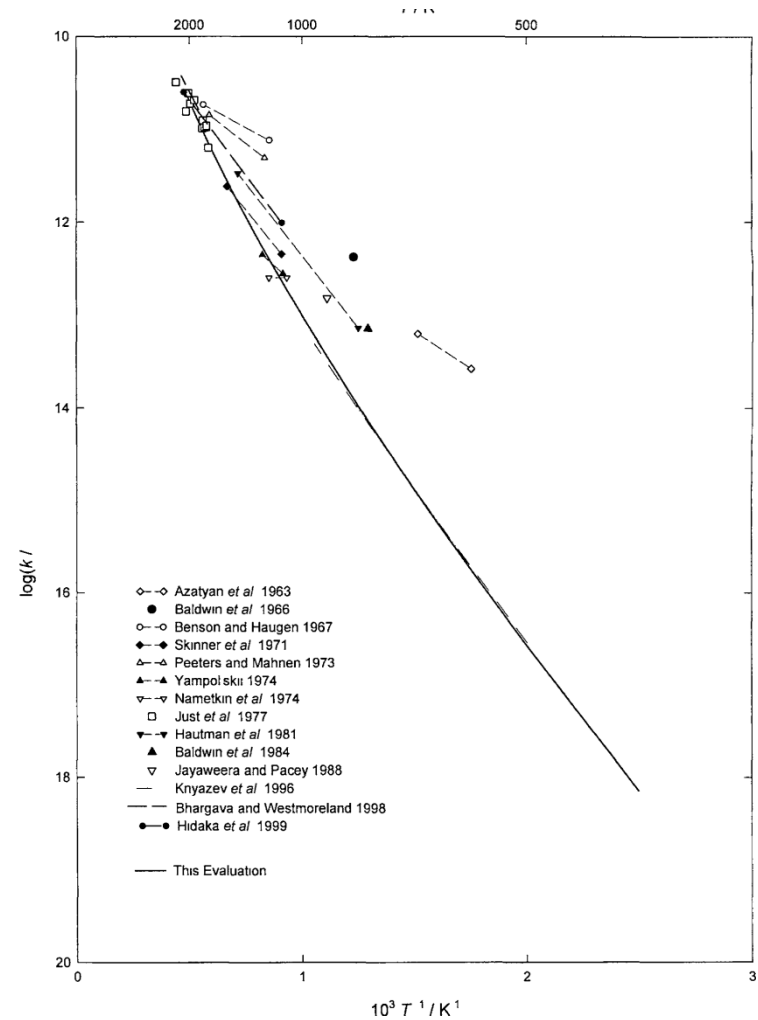


Preferred Values

$k = 3.9 \cdot 10^{-22} T^{3.62} \exp(-5670/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
over the range 400–2000 K.

Reliability

$\Delta \log k = \pm 0.4$ over the range 400–2000 K.



Nagy and Turanyi, Uncertainty of Arrhenius Parameters
Int J Chem Kinet 43: 359-378, 2011

- Analytical expression is derived that describes the temperature dependence of the uncertainty of k as a function of the elements of the covariance matrix of the Arrhenius parameters.
- Recommendations are given for an improved representation of the uncertainty information in future chemical kinetics databases using the covariance matrix of the Arrhenius parameters
- method suggested for determination of covariance matrix and joint probability density function of Arrhenius parameters from the present uncertainty information given in the kinetics databases.

T dependent uncertainty parameter,

$$k = AT^n \exp(-E/RT)$$

- Covariance matrix:

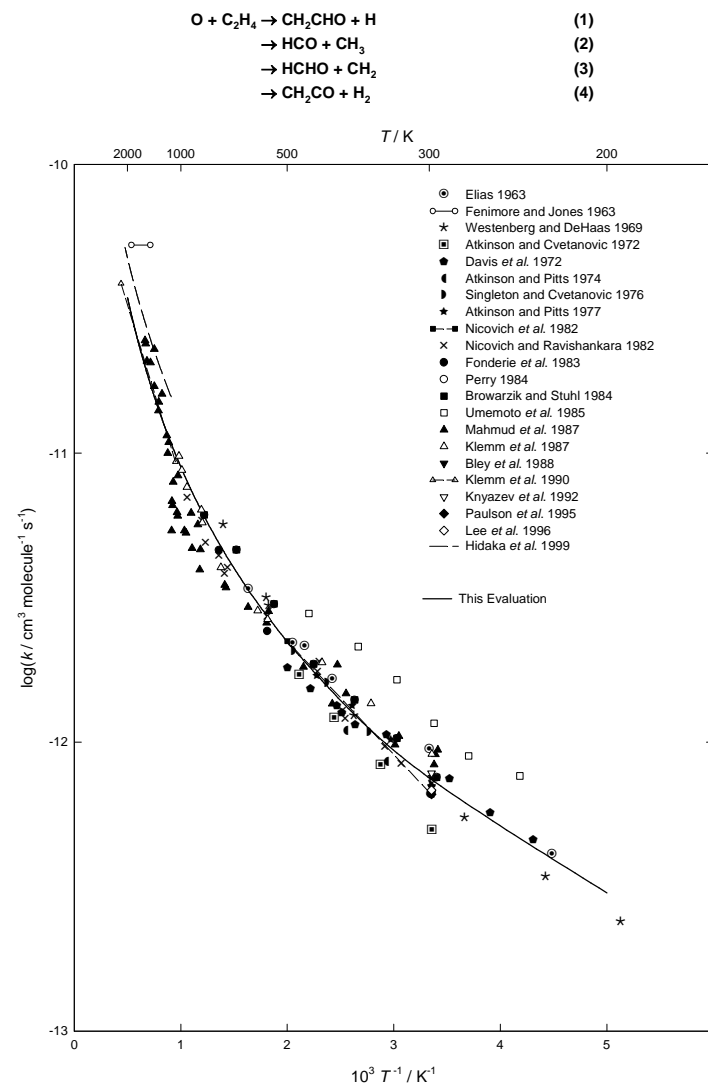
$$\begin{aligned}\Sigma_p &= \overline{(\mathbf{p} - \bar{\mathbf{p}}) (\mathbf{p} - \bar{\mathbf{p}})^T} \\ &= \begin{bmatrix} \sigma_\alpha^2 & r_{\alpha n} \sigma_\alpha \sigma_n & r_{\alpha \varepsilon} \sigma_\alpha \sigma_\varepsilon \\ r_{\alpha n} \sigma_\alpha \sigma_n & \sigma_n^2 & r_{n \varepsilon} \sigma_n \sigma_\varepsilon \\ r_{\alpha \varepsilon} \sigma_\alpha \sigma_\varepsilon & r_{n \varepsilon} \sigma_n \sigma_\varepsilon & \sigma_\varepsilon^2 \end{bmatrix}\end{aligned}$$

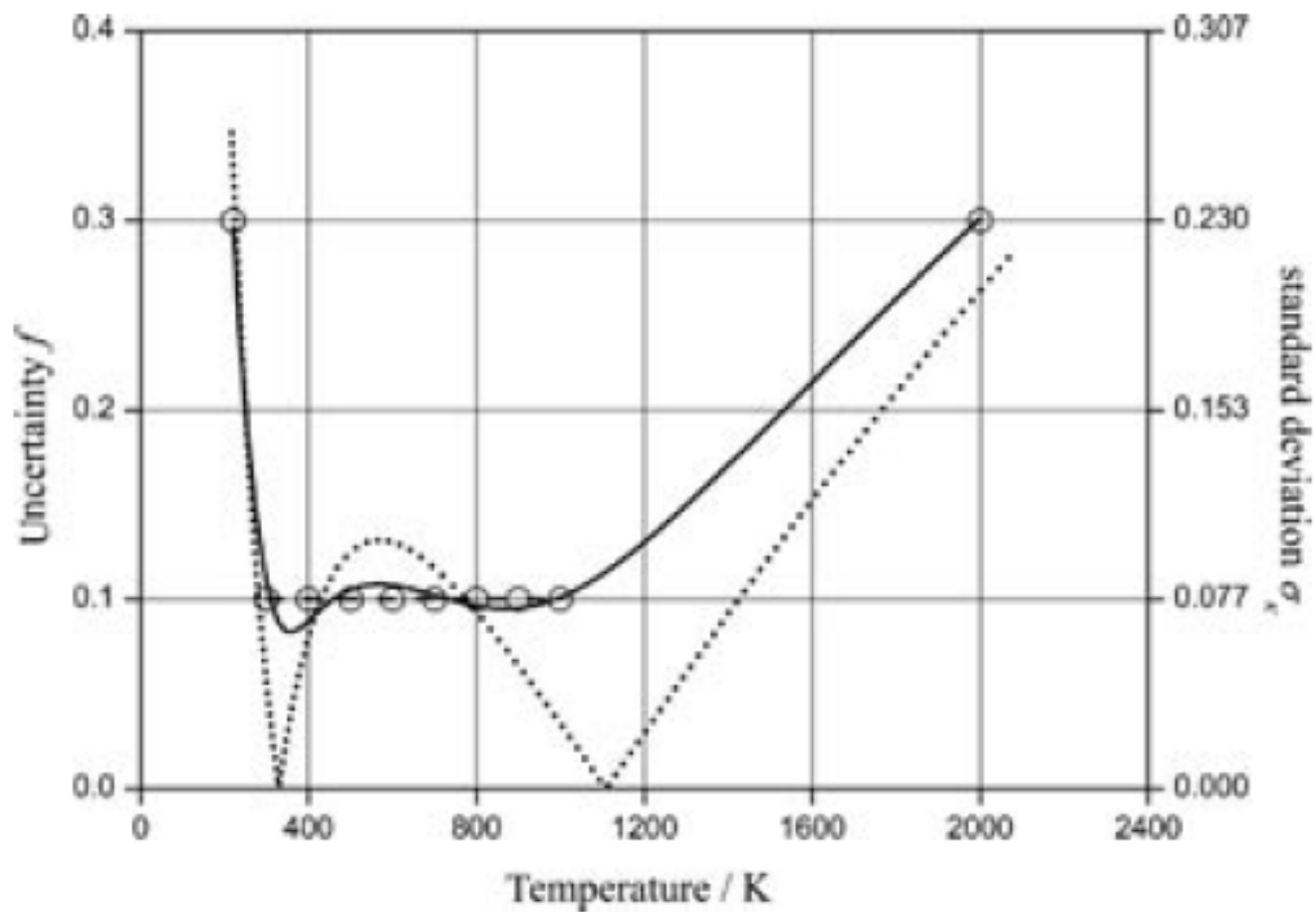
- Uncertainty parameter ($M = 3/\ln 10$ or $2/\ln 10$) depending on definition of reliability in evaluation

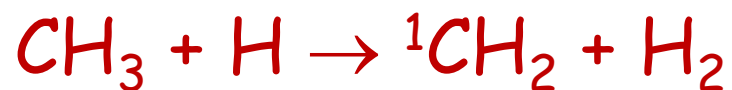
$$F(T) = M \sqrt{\sigma_\alpha^2 + \sigma_n^2 \ln^2 T + \sigma_\varepsilon^2 T^{-2} + 2r_{\alpha n} \sigma_\alpha \sigma_n \ln T - 2r_{\alpha \varepsilon} \sigma_\alpha \sigma_\varepsilon T^{-1} - 2r_{n \varepsilon} \sigma_n \sigma_\varepsilon T^{-1} \ln T}$$

O + C₂H₄: evaluation

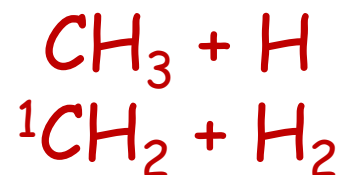
- $k = 2.25 \cdot 10^{-17} T^{1.88} \exp(-92/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 220-2000 K.
- Reliability
 $\Delta \log k = \pm 0.1$ over the range 300-1000 K, rising to ± 0.3 at 220 K and 2000 K







- $k = 2.1 \cdot 10^{-8} T^{-0.56} \exp(-8000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 300-2500 K.
- Reliability
 $\Delta \log k = \pm 0.15$ over the range 300-1000 K, ± 0.3 over the range 1000-1700 K, and ± 0.2 over the range 1700-2500 K.
- Comments on Preferred Values
The values of k obtained in the shock tube studies of Bhaskaran *et al.*¹ and Davidson *et al.*³ are in reasonable agreement and also agree to within a factor of ~ 3 with the rate constants predicted by combining the thermodynamic data with the low temperature data on the reverse reaction, whereas the value of k obtained in the flame study of Langley and Burgess² seems unacceptably high.



$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	T/K	Reference	Comments
<i>Rate Coefficient Measurements</i>			
$3.0 \cdot 10^{-10} \exp(-7580/T)$	1700–2300	Bhaskaran, Frank, and Just, 1980 ¹	(a)
$1.7 \cdot 10^{-11}$	1810	Langley and Burgess, 1989 ²	(b)
$4.1 \cdot 10^{-10} \exp(-6884/T)$	1850–2100	Davidson <i>et al.</i> , 1995 ³	(c)
<i>Reviews and Evaluations</i>			
$1.0 \cdot 10^{-10} \exp(-7600/T)$	300–2500	CEC, 1992; 1994 ⁴	(d)

Rate Coefficient Measurements

$1.3 \cdot 10^{-10}$	298	Ashfold <i>et al.</i> , 1981 ¹	(a)
$1.1 \cdot 10^{-10}$	298	Langford, Petek, and Moore, 1983 ²	(b)
$7.0 \cdot 10^{-11} \exp(160/T)$	210–475	Wagener, 1990 ³	(c)
$1.0 \cdot 10^{-10}$	295–859	Hancock and Heal, 1992 ⁴	(d)
$k_1 = 2.2 \cdot 10^{-10}$	1850–2100	Davidson <i>et al.</i> , 1995 ³	(e)

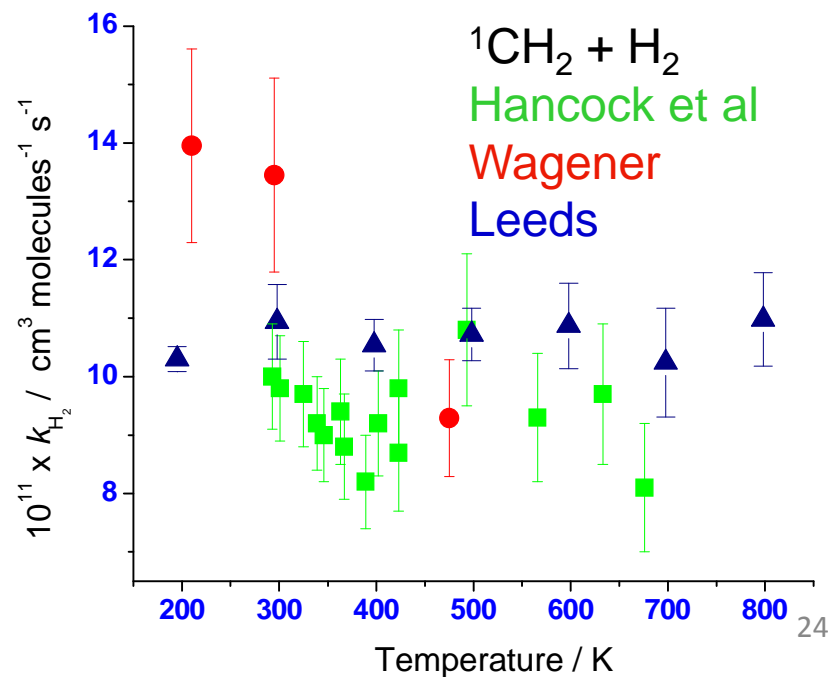
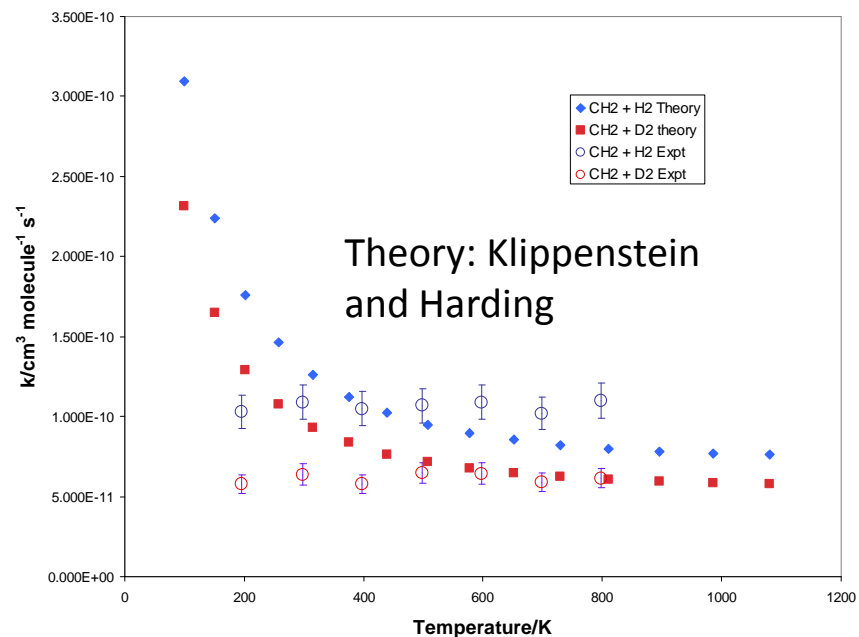
Branching Ratios

$k_1/k > 0.8$	298	Braun, Bass, and Pilling, 1970 ⁶	(f)
$k_2/k = 0.1$	298	Blitz, Pilling, and Seakins, 2001 ⁷	(g)



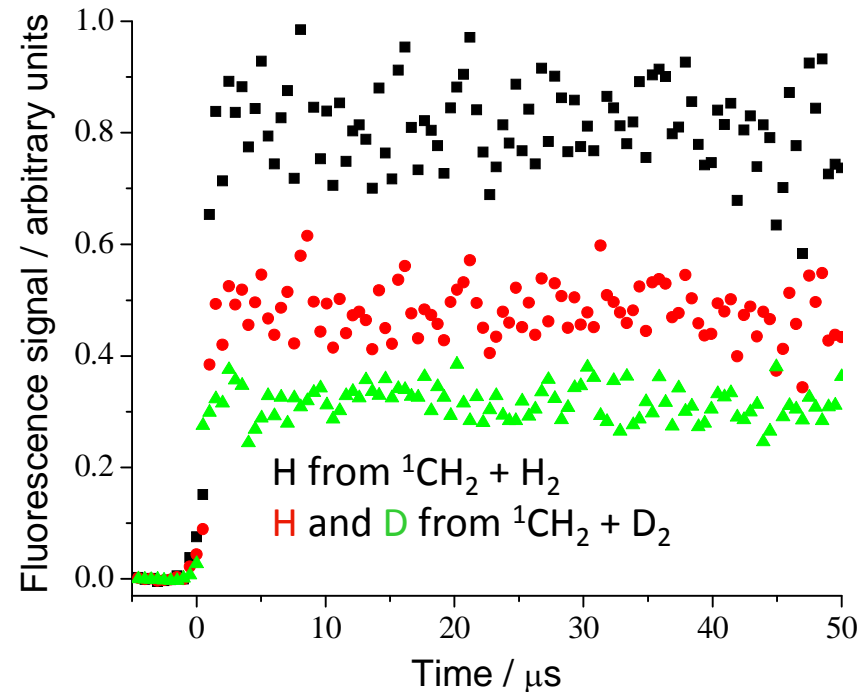
T / K	$10^{10} \times k_{\text{H}_2} / \text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$	$10^{11} \times k_{\text{D}_2} / \text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
195	1.030 ± 0.021	5.77 ± 0.27
298	1.094 ± 0.064	6.39 ± 0.47
398	1.054 ± 0.044	5.77 ± 0.36
498	1.072 ± 0.045	6.49 ± 0.52
598	1.087 ± 0.073	6.45 ± 0.44
698	1.024 ± 0.093	5.91 ± 0.22
798	1.098 ± 0.080	6.14 ± 0.35

From yesterday



Absolute H and D atom yields from ${}^1\text{CH}_2 + \text{H}_2, \text{D}_2$

- k_{CIISC} again increases as T decreases. Similar behaviour for both collision partners.
- H vs D yields depend on dissociation of CH_2D_2^* . Theory gives a lower H:D ratio (~ 1.3 vs $1.6 - 2$)



T / K	${}^1\text{CH}_2 + \text{H}_2$	${}^1\text{CH}_2 + \text{D}_2$		
	a_{H}	a_{H}	a_{D}	$a_{\text{H}} + a_{\text{D}}$
195	0.71 ± 0.07	0.49 ± 0.07	0.24 ± 0.09	0.73 ± 0.12
298	0.85 ± 0.08	0.47 ± 0.05	0.28 ± 0.09	0.75 ± 0.10
398	0.92 ± 0.08	0.55 ± 0.07	0.34 ± 0.04	0.89 ± 0.10 ²⁵

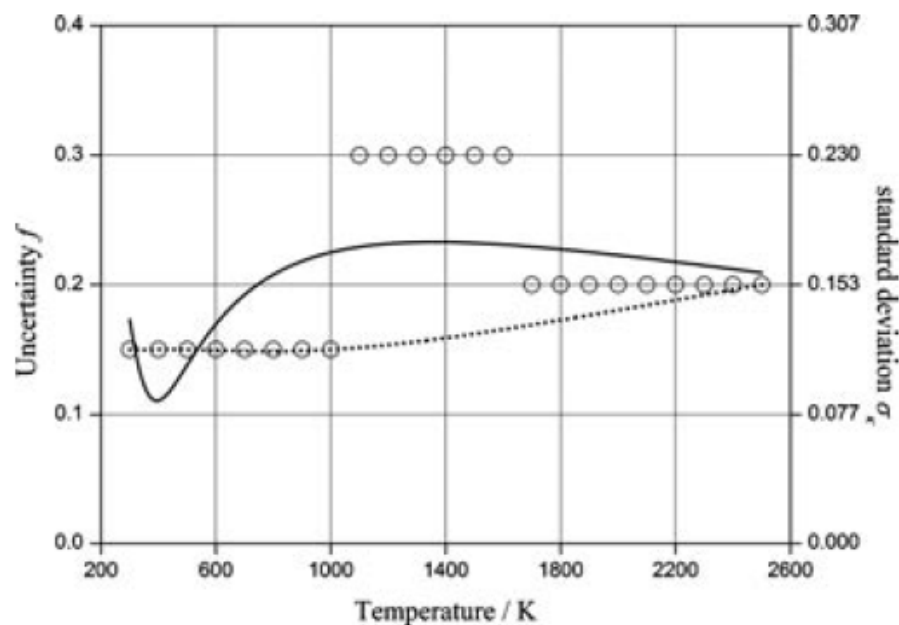
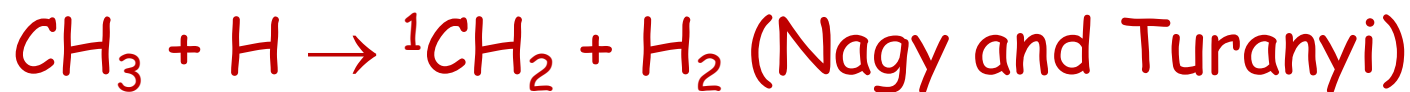


Figure 7 Uncertainties of reaction R5 are defined [14] in three temperature intervals and the uncertainty–temperature function was fitted to the values represented by the circles. The best least squares fit (solid line; see row **R5** in Table IV) does not approach these points well, because the recommended uncertainties were not consistent. The alternatively proposed $f(T)$ curve (dotted line) remains below all uncertainty points and has the highest average value of $\sigma_k^2(T)$ in the inverse temperature interval of $[1/T_2, 1/T_1]$ (see text and row **R5m** in Table IV).