IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC11

This data sheet evaluated 16th October 2007 (with no revision of preferred values).

$HO + HCHO \rightarrow H_2O + HCO$

$\Delta H° = -127.3$ kJ·mol^{-1}

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$1.25 \times 10^{-11} \exp[-(88 \pm 151)/T]$	299-426	Atkinson and Pitts, 1978	FP-RF
$(9.4 \pm 1.0) \times 10^{-12}$	299		
$(1.05 \pm 0.11) \times 10^{-11}$	228-362	Stief et al., 1980	FP-RF
$(9.86 \pm 1.13) \times 10^{-12}$	298		
$(8.1 \pm 1.7) \times 10^{-12}$	296	Temps and Wagner, 1984	DF-LMR
$1.66 \times 10^{-11} \exp[-(86 \pm 40)/T]$	296-576	Zabarnick et al., 1988	PLP-LIF
$(1.25 \pm 0.11) \times 10^{-11}$	298 ± 3		
$(7.95^{+2.04}_{-1.44}) \times 10^{-12}$	298	Yetter et al., 1989	DF-RF
$(1.94 \pm 0.30) \times 10^{-11}$	1205 ± 16	Bott and Cohen, 1991	SH-RA
$9.52 \times 10^{-18} T^{2.03} \exp(636/T)$	202-399	Sivakumaran et al., 2003	PLP-LIF (a)
$(8.46 \pm 0.5) \times 10^{-12}$	298		
Relative Rate Coefficients			
$(8.40 \pm 0.51) \times 10^{-12}$	299 ± 2	Niki et al., 1984	RR (b)

Comments

(a) The authors combined their data with previous room temperature data of Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984), Niki et al. (1984), Zabarnick et al. (1988) and Yetter et al. (1989) to obtain a 298 K rate coefficient of $k = 8.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} and a temperature-dependent expression of $k = 9.65 \times 10^{-18} T^{2.03} \exp(636/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200-400 K. Using resonance fluorescence detection of H atoms, an upper limit of 4% was determined for the production of H atoms at 298 K.

(b) HO radicals were generated by the photolysis of methyl or ethyl nitrite in air, and the concentration of $^{13}CH_2O$ and ethene (the reference compound) were measured by FTIR absorption spectroscopy during the experiments. The measured rate coefficient ratio of $k(HO + {}^{13}CH_2O)/k(HO + \text{ethene}) = 0.99 \pm 0.06$ is placed on an absolute basis by use of a rate coefficient of $k(HO + \text{ethene}) = 8.48 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 299 K and atmospheric pressure (Atkinson and Arey, 2003).

Preferred Values

$k = 8.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K.
$k = 5.4 \times 10^{-12} \exp(135/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
$\Delta(E/R) = \pm 100$ K.

Comments on Preferred Values

The absolute rate coefficients of Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984), Yetter et al. (1989) and Sivakumaran et al. (2003) and the relative rate coefficient of Niki et al. (1984) at 299 ± 2 K are in good agreement (to within ~20% or better at any given temperature) over the temperature range common to two or more of these studies (228-399 K). The absolute rate coefficients of Zabarnick et al. (1988) over the temperature range 296-378 K are consistently higher than those of Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984), Niki et al. (1984), Yetter et al. (1989) and Sivakumaran et al. (2003), and are not used in the evaluation.

The absolute rate coefficients of Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984), Yetter et al. (1989) and Sivakumaran et al. (2003), and the relative rate coefficient of Niki et al. (1984) for formaldehyde-^{13}C, have been fitted to the three parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 1.25 \times 10^{-17}\ T^2 \exp(615/T)$ cm^3 molecule^{-1} s^{-1} over the temperature range 202-426 K. This expression yields rate coefficients which are within 3% of those calculated from the three parameter expression recommended by Sivakumaran et al. (2003) for the temperature range 200-430 K [see comment (a) above], and predicts a rate coefficient at 1205 K a factor of 1.56 higher that that measured by Bott and Cohen (1991). The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 240 K and is derived from the three parameter expression with $A = C\,e^2\,T^2$ and $B = D + 2T$. Note that the preferred Arrhenius expression should not be used outside of the specified temperature range (200-300 K); rather the full three parameter expression should be used.

D-atom, ^{13}C and ^{18}O isotope effects have been measured for the reactions of HO radicals with HCHO, HCDO, DCDO, H^{13}CHO and HCH^{18}O at 298 ± 2 K (D'Anna et al., 2003; Feilberg et al., 2004). The product data of Temps and Wagner (1984), Niki et al. (1984) and Sivakumaran et al. (2003) and the kinetic/modeling results of Yetter et al. (1989) show that at 298 K this reaction yields H_2O + HCO, as also concluded by Butkovskaya and Setser (1998) from an infrared chemiluminescence study of the reaction at 0.67-1.3 mbar pressure.

References

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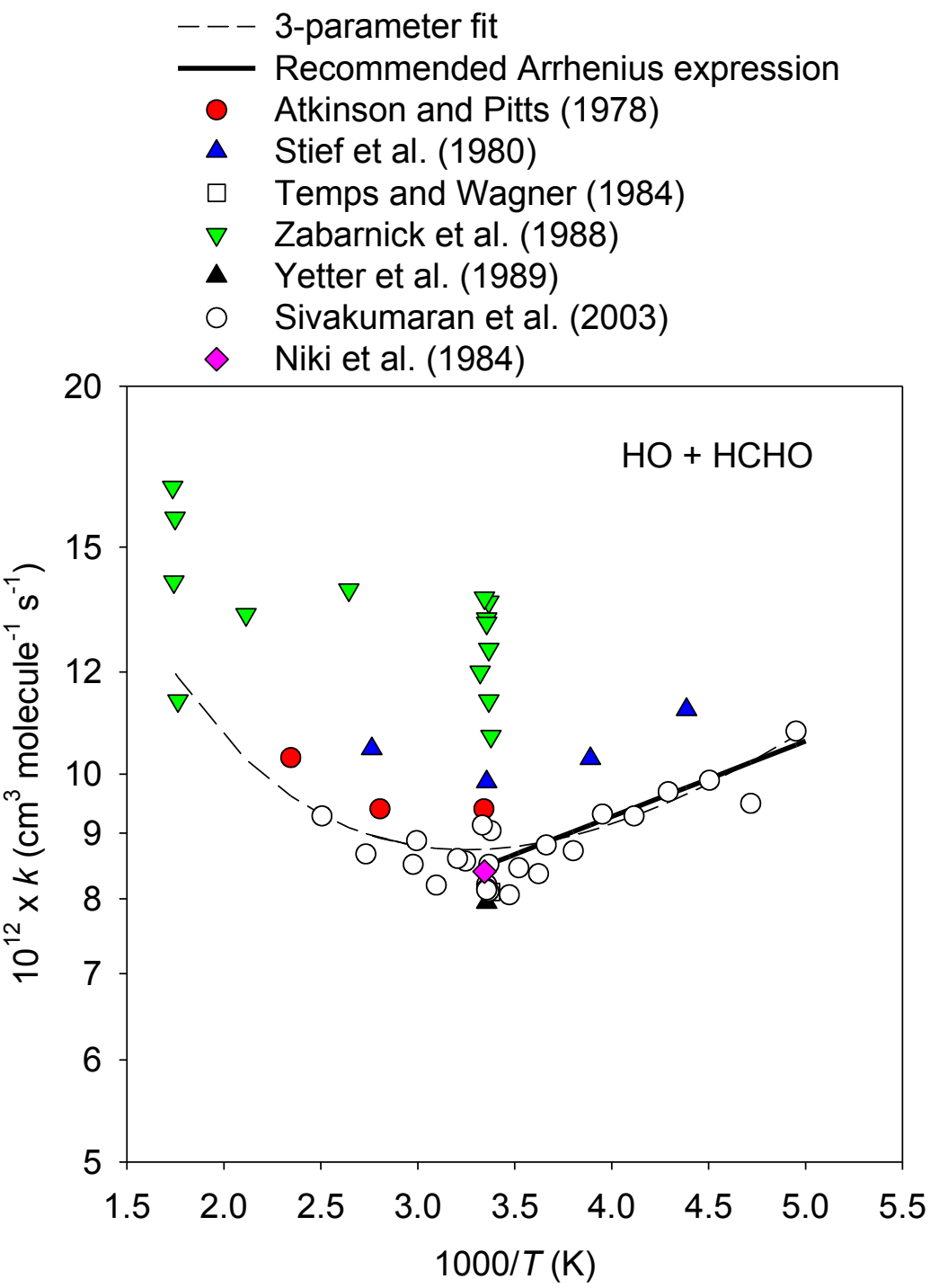
3-parameter fit
Recommended Arrhenius expression
Atkinson and Pitts (1978)
Stief et al. (1980)
Temps and Wagner (1984)
Zabarnick et al. (1988)
Yetter et al. (1989)
Sivakumaran et al. (2003)
Niki et al. (1984)
HO + HCHO
10^{12} x k (cm^3 $molecule^{-1}$ s^{-1})
1000/T (K)
20
15
12
10
9
8
7
6
5
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5