IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet II.A2.7 HOx_VOC5

This data sheet last evaluated: December 2005.

$HO + C_3H_6 + M \rightarrow C_3H_6OH + M$

$\Delta H° = -134$ kJ·mol^{-1}

Low-pressure rate coefficients
Rate coefficient data

k_0/cm^3 molecule^{-1} s^{-1}	Temp./K	*Reference*	Technique/ Comments
Absolute Rate Coefficients			
8 x 10^{-28} [Ar]	298	Zellner and Lorenz, 1983	PLP-RF (a)
9 x 10^{-28} [N_2]	298	Vakhtin et al., 2003	PLP-LIF (b)
Relative Rate Coefficients			
8 x 10^{-27} [Ar] 8 x 10^{-27} [air]	298	Klein et al., 1984	(c)

Comments

(a) Pressure range 1.3 mbar to 170 mbar. Falloff behavior detected, and evaluated with $F_c = 0.8$. Rough estimate of k_0 because of the only limited extent of observed falloff.

(b) Experiments with pulsed Laval nozzle supersonic expansion over the range 2 x 10^{-16} ≤ [N_2] ≤ 3 x 10^{18} molecule cm^{-3} at 296 K. Single experiments at (2-3) x 10^{16} molecule cm^{-3} also at 96, 103, and 165 K. Rough estimate of k_0 because of limited extent of observed falloff. Falloff curves constructed with $F_c = 0.5$ and k_∞ (296 K) = 3.0 x 10^{-11} cm^3 molecule^{-1} s^{-1}. See also comment (d) for k_∞.

(c) HO_2NO_2-NO system used as source of HO radicals. Reaction studied relative to HO + *n*-hexane, with the latter reaction calibrated against absolute measurements of the reaction HO + *n*-butane (k = 2.53 x 10^{-12} cm^3 molecule^{-1} s^{-1} at 295 K). Pressure range 1.3 mbar to 1000 mbar; falloff effects could be detected. Evaluation with $F_c = 0.5$ gives the present k_0 value. Rough estimate of k_0 because of the only limited extent of observed falloff.

Preferred Values

$k_0 = 8 \times 10^{-27} (T/300)^{-3.5}$ [N_2] cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K.

Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

The uncertainty of the extrapolated k_0 is large, because the reaction is close to the high-pressure limit at pressures. The preferred values follow the falloff extrapolation from ref. 2 which shows the smallest scatter. Falloff extrapolations are made using $F_c = 0.5$ at 300 K. The temperature coefficient of k_0 is estimated by analogy to the reaction HO + C_2H_4 + M → C_2H_4OH + M.

High-pressure rate coefficients
Rate coefficient data

k_∞/cm^3 molecule^{-1} s^{-1}	Temp./K	*Reference*	Technique/ Comments
Absolute Rate Coefficients			
$(3.0 \pm 0.5) \times 10^{-11}$	298	Zellner and Lorenz, 1984	PLP-RF (a)
$(2.95 \pm 0.1) \times 10\text{-}11(T/300)^{-1.06}$	95-296	Vakhtin et al., 2003	PLP-LIF (b)
Relative Rate Coefficients			
$(3.0 \pm 0.2) \times 10^{-11}$	295	Klein et al., 1984	(c)
$(8.1 \pm 1.8) \times 10^{-11}$	103	Vakhtin et al., 2001	(d)

Comments

(a) See comment (a) for k_0.
(b) See comment (b) for k_0.
(c) See comment (c) for k_0.
(d) Pulsed Laval nozzle supersonic expansion of nitrogen with admixed reactants. OH generated by photolysis of H_2O_2 or reaction of O(^{1}D) with *n*-butane after photolysis of N_2O. [N_2] = 2.1 x 10^{16} molecule cm^{-3}. Reaction observed very close to the high pressure limit.

Preferred Values

$k = 2.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 298 K and 1 bar of air.
$k_\infty = 3.0 \times 10^{-11} (T/300)^{-1}$ cm^3 molecule^{-1} s^{-1} over the range 200-300 K.

Reliability

$\Delta \log k_\infty = \pm 0.1$ over the temperature range 200 K to 300 K.
$\Delta n = \pm 1$.

Comments on Preferred Values

The preferred values are based on Zellner and Lorenz (1984), Klein et al. (1984), Vakhtin et al. (2003), Nielsen et al. (1990) and Tully and Goldsmith (1985). There is an uncertainty about the extent of falloff at temperatures above 300 K and there is the possibility of a small activation barrier, such as observed in the reaction HO + C_2H_2 + M → C_2H_2OH + M. The preferred temperature dependence is derived by combining the results from Zellner and Lorenz (1984), Klein et al. (1984) and Vakhtin et al. (2003), confirming the suggestions from Atkinson (1994) and Tsang (1991). $F_c = 0.5$ serves for estimating the extent of falloff.

The following text-line combines the preferred values for the high and low pressure limiting rate coefficients to generate a single, cut-and-paste expression for calculation of *k*:

=((8e-27*(*T*/300)^-3.5)*M*(3.0e-11*(*T*/300)^-1))/((8e-27*(*T*/300)^-3.5)*M+(3.0e-11*(*T*/300)^-1))*10^(log10(0.5)/(1+(log10((8e-27*(*T*/300)^-3.5)*M/(3.0e-11*(*T*/300)^-1))/(0.75-1.27*log10(0.5)))^2))

The molecular density, $M = 7.243 \times 10^{21} P(bar)/T(K)$

References

Atkinson, R.: J. Phys. Chem. Ref. Data, Monograph 2, 82, 1994.
Klein, Th., Barnes, I., Becker, K. H., Fink, E. H. and Zabel, F.: J. Phys. Chem. 88, 5020, 1984.
Nielsen, O. J., Jørgensen, O., Donlon, M., Sidebottom, H. W., O'Farrell, D. J. and Treacy, J.: Chem. Phys. Lett 168, 319, 1990.
Tsang, W.: J. Phys. Chem. Ref. Data 20, 221, 1991.
Tully, F. P. and Goldsmith, J. E. M.: Chem. Phys. Lett. 116, 345, 1985.
Vakhtin, A. B., Lee, S., Heard, D. E., Smith, I. W. M. and Leone, S. R.: J. Phys. Chem. A 105, 7889, 2001.
Vakhtin, A. B., Murphy, J. E. and Leone, S. R.: J. Phys. Chem. A, 107, 10055, 2003.
Zellner, R. and Lorenz, K.: J. Phys. Chem. 88, 984, 1984.