# Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC26

Website: http://iupac.pole-ether.fr. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission. This data sheet last evaluated: 2nd August 2007; no revision of preferred values.

$$HO + CH_3CH(OH)CH_3 \rightarrow H_2O + (CH_3)_2CHO \qquad (1)$$
$$\rightarrow H_2O + CH_3C(OH)CH_3 \qquad (2)$$
$$\rightarrow H_2O + CH_3CH(OH)CH_2 \qquad (3)$$
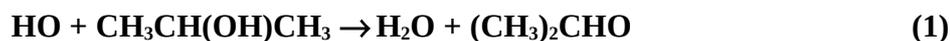
$\Delta H°(1) = -58.8$ kJ·mol$^{-1}$

## Rate coefficient data ($k = k_1 + k_2 + k_3$)

| $k$/cm$^3$ molecule$^{-1}$ s$^{-1}$ | Temp./K | Reference | Technique/ Comments |
|---|---|---|---|
| *Absolute Rate Coefficients* | | | |
| $(5.48 \pm 0.55) \times 10^{-12}$ | $296 \pm 2$ | Overend and Paraskevopoulos, 1978 | FP-RA |
| $5.8 \times 10^{-12}$ exp[$-(30 \pm 90)/T$] | 240-440 | Wallington and Kurylo, 1987 | FP-RF |
| $(5.81 \pm 0.34) \times 10^{-12}$ | 296 | | |
| $(5.69 \pm 1.09) \times 10^{-12}$ | $298 \pm 2$ | Nelson et al., 1990 | PR-RA |
| $1.044 \times 10^{-17} T^{1.86}$ exp($736/T$) | 293-587 | Dunlop and Tully, 1993 | PLP-LIF (a) |
| $(5.10 \pm 0.21) \times 10^{-12}$ | 293 | | |
| $2.80 \times 10^{-12}$ exp[$(184 \pm 40)/T$] | 253-372 | Yujing and Mellouki, 2001 | PLP-LIF |
| $(5.17 \pm 0.23) \times 10^{-12}$ | 298 | | |
| | | | |
| *Relative Rate Coefficients* | | | |
| $(5.38 \pm 0.70) \times 10^{-12}$ | $298 \pm 2$ | Nelson et al., 1990 | RR (b) |

## Comments

(a) The reactions of H$^{16}$O radicals were studied over the temperature range 293 K to 745 K and the reactions of H$^{18}$O radicals were studied at 548 K and 587 K. Non-exponential decays of H$^{16}$O radicals were observed over the temperature range 504 K to 600 K and, while exponential H$^{16}$O radical decays were observed above 600 K, the rate coefficients were significantly lower than expected from extrapolation of the lower temperature data. These observations are consistent with thermal decomposition of the CH$_3$CH(OH)CH$_2$ radical formed in reaction channel (3) [the same radical as formed from HO radical addition to propene] at temperatures >500 K. Hence using H$^{16}$O radicals, values of ($k_1 + k_2 + k_3$) were measured at temperatures ≤ 500 K and ($k_1 + k_2$) at temperatures >600 K. No regeneration of H$^{18}$O radicals from thermal decomposition of the CH$_3$CH($^{16}$OH)CH$_2$ radical can occur, and hence the measured H$^{18}$O rate coefficients are those for ($k_1 + k_2 + k_3$).

(b) HO radicals were generated by the photolysis of CH$_3$ONO in air. The concentrations of 2-propanol and cyclohexane (the reference organic) were measured by GC. The measured rate coefficient ratio $k$(HO + 2-propanol)/$k$(HO + cyclohexane) is placed on an absolute basis by use of a rate coefficient of $k$(HO + cyclohexane) = $6.97 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K (Atkinson, 2003).

## Preferred Values

$k = 5.1 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K.

$k = 2.6 \times 10^{-12}$ exp(200/$T$) cm$^3$ molecule$^{-1}$ s$^{-1}$ over the temperature range 250-360 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 measured by Dunlop and Tully (1993) and Yujing and Mellouki (2001) are in excellent agreement over the temperature range common to both studies (293-378 K), and the preferred rate coefficients are derived from these two studies (Dunlop and Tully, 1993; Yujing and Mellouki, 2001). The H$^{18}$O rate coefficients at 548 K and 587 K and the H$^{16}$O rate coefficients at $\leq$ 502 K obtained by Dunlop and Tully (1993) and the rate coefficients of Yujing and Mellouki (2001) (253-372 K) were fitted to the three parameter expression $k = CT^2$ exp(-$D/T$), resulting in $k = 4.03 \times 10^{-18}\ T^2$ exp(792/$T$) cm$^3$ molecule$^{-1}$ s$^{-1}$ over the temperature range 253-587 K. The preferred Arrhenius expression, $k = A$ exp(-$B/T$), is centered at 295 K and is derived from the three parameter expression with $A = C\ e^2\ T^2$ and $B = D + 2T$. The preferred rate coefficients are within 15% of those measured by Wallington and Kurylo (1987) over the temperature range 250-360 K, and are in agreement within the cited error limits with the room temperature absolute and relative rate coefficients of Overend and Paraskevopoulos (1978) and Nelson et al. (1990).

## References

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Nelson, L., Rattigan, O., Neavyn, R., Sidebottom, H., Treacy, J. and Nielsen, O. J.: Int. J. Chem. Kinet. 22, 1111, 1990.

Overend, R. and Paraskevopoulos, G.: J. Phys. Chem. 82, 1329, 1978.

Wallington, T. J. and Kurylo, M. J.: Int. J. Chem. Kinet. 19, 1015, 1987.

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