

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC41

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This data sheet last evaluated: 30th July 2007; no revision of preferred values.

HO + 2-C₃H₇ONO₂ → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
4.3 x 10 ⁻¹² exp(-1250/ <i>T</i>) + 2.5 x 10 ⁻¹³ exp(-32/ <i>T</i>)	233-395	Talukdar et al., 1997	PLP-LIF (a)
(2.88 ± 0.19) x 10 ⁻¹³	298		
<i>Relative Rate Coefficients</i>			
(1.68 ± 0.42) x 10 ⁻¹³	299 ± 2	Atkinson et al., 1982	RR (b)
(5.3 ± 2.1) x 10 ⁻¹³	295 ± 2	Becker and Wirtz, 1989	RR (c)
(3.83 ± 0.49) x 10 ⁻¹³	298 ± 2	Atkinson and Aschmann, 1989	RR (d)

Comments

- Experiments were carried out as a function of total pressure and with different diluent gases (133 mbar He to 400 mbar SF₆) and with up to 80 mbar O₂ present. No effect of pressure, diluent gas or presence or absence of O₂ on the measured rate coefficients were observed. Rate coefficients for the reactions of H¹⁸O and DO radicals with 2-propyl nitrate were also measured over the temperature ranges 233-298 K and 230-403 K, respectively, with 298 K rate coefficients of (3.15 ± 0.20) x 10⁻¹³ cm³ molecule⁻¹ s⁻¹ and (3.6 ± 0.4) x 10⁻¹³ cm³ molecule⁻¹ s⁻¹, respectively.
- HO radicals were generated from the photolysis of CH₃ONO in ~1 bar air at >300 nm. Experiments were carried out in an ~75 liter Teflon chamber, and concurrent photolysis of 2-propyl nitrate was indicated from the data analysis. The concentrations of 2-propyl nitrate and cyclohexane (the reference organic) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + 2\text{-propyl nitrate})/k(\text{HO} + \text{cyclohexane}) = 0.024 \pm 0.006$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 7.00 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 299 K (Atkinson, 2003).
- HO radicals were generated from the photolysis of CH₃ONO in 1 bar air at 280 nm to 450 nm. Experiments were carried out in a 36.5 liter quartz chamber, and photolysis of 2-propyl nitrate was indicated from the data analysis. The concentrations of 2-propyl nitrate and *n*-butane (the reference organic) were measured by GC-MS and GC, respectively. The measured rate coefficient ratio of $k(\text{HO} + 2\text{-propyl nitrate})/k(\text{HO} + n\text{-butane}) = 0.23 \pm 0.09$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + n\text{-butane}) = 2.30 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (IUPAC, 2007).
- HO radicals were generated by the photolysis of CH₃ONO in ~1 bar air at >300 nm. Experiments were carried out in a 6400 liter Teflon chamber. The concentrations of 2-propyl nitrate and cyclohexane (the reference organic) were measured by GC, and irradiations in the absence of CH₃ONO allowed the photolysis of 2-propyl nitrate to be accurately taken into account in the data

analysis. The measured rate coefficient ratio of $k(\text{HO} + 2\text{-propyl nitrate})/k(\text{HO} + \text{cyclohexane}) = 0.055 \pm 0.007$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003). This study supersedes the earlier study of Atkinson et al. (1982).

Preferred Values

$k = 2.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 6.2 \times 10^{-13} \exp(-230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230-300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta(E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the absolute 233-300 K rate coefficients of Talukdar et al. (1997). The extensive study of Talukdar et al. (1997) provided no evidence for the rate coefficient k to depend on total pressure, nature of the diluent gas, or the presence of O_2 at pressures up to 80 mbar (60 Torr). Additionally, the use of DO radicals showed no evidence for the formation of HO radicals as a reaction product. However, as noted in the data sheets for the reactions of the HO radical with CH_3ONO_2 and $\text{C}_2\text{H}_5\text{ONO}_2$ (IUPAC, 2005), the experiments of Talukdar et al. (1997) were not actually carried out in air at 1 bar total pressure.

Arrhenius plots of the rate coefficients for the reactions of HO, H^{18}O and DO radicals with 2-propyl nitrate exhibit significant curvature (especially pronounced for the DO radical reaction for which the measured rate coefficient was independent of temperature over the range 230-269 K). The measured temperature dependencies at around 298 K and below are quite small. The room temperature relative rate coefficient of Atkinson and Aschmann (1989) (which supersedes the earlier data of Atkinson et al., 1982) is 33% higher than the recommended 298 K rate coefficient, which may be considered reasonable agreement because of the low rate coefficient (on the low end of those reported by that research group) and hence small fraction of 2-propyl nitrate reacted during the experiments. The relative rate coefficient of Becker and Wirtz (1989) is almost a factor of 2 higher than the recommendations, but has high cited uncertainties.

We attach rather large uncertainties to the recommended values of the 298 K rate coefficient and E/R until the data of Talukdar et al. (1997) are confirmed by absolute techniques in air at 1 bar pressure.

References

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