

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO₃_VOC14

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This data sheet updated: 18th October 2007 (with no revisions to the preferred values).

NO₃ + CH₃CH₂CH₂CHO → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1.26 x 10 ⁻¹² exp(-1478/ <i>T</i>) (1.1 ± 0.1) x 10 ⁻¹⁴	267-332 296	Ullerstam et al., 2000	DF-RA (a)
7.6 x 10 ⁻¹¹ exp[-(2466 ± 505)/ <i>T</i>] (1.46 ± 0.16) x 10 ⁻¹⁴	298-433 298 ± 2	Cabañas et al., 2001	DF-LIF
(1.19 ± 0.14) x 10 ⁻¹⁴	301 ± 2	Bossmeyer et al., 2006	DOAS/GC (b)
<i>Relative Rate Coefficients</i>			
(1.09 ± 0.09) x 10 ⁻¹⁴	298 ± 2	D'Anna and Nielsen, 1997	RR (c)
(1.04 ± 0.11) x 10 ⁻¹⁴	297 ± 2	Ullerstam et al., 2000	RR (d)
(1.15 ± 0.06) x 10 ⁻¹⁴	296 ± 2	Papagni et al., 2001	RR (e)
(1.23 ± 0.11) x 10 ⁻¹⁴	298 ± 2	D'Anna et al., 2001	RR (c)

Comments

- Carried out in the presence of 20% O₂ in the diluent gas to minimize secondary reactions (experiments in the absence of O₂ yielded rate coefficients a factor of ~3 higher¹). The Arrhenius expression cited in the table is obtained from a least-squares analysis of the measured rate coefficients at 267 K, 296 K and 332 K.
- Carried out in the EUPHORE chamber at atmospheric pressure of air. NO₃ radical concentrations were measured by DOAS, and butanal concentrations by GC.
- NO₃ radicals were generated by the thermal dissociation of N₂O₅. Experiments were carried out in 1 atmosphere of air with measurements of butanal and 1-butene (the reference compound) by FTIR spectroscopy. The measured rate coefficient ratios $k(\text{NO}_3 + \text{butanal})/k(\text{NO}_3 + 1\text{-butene}) = 0.81 \pm 0.06$ (D'Anna and Nielsen, 1997) and 0.91 ± 0.08 (D'Anna et al., 2001) are placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + 1\text{-butene}) = 1.35 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 1997).
- NO₃ radicals were generated by the thermal dissociation of N₂O₅. Experiments were carried out in 1 atmosphere of synthetic air or N₂ with measurements of butanal and propene (the reference compound) by FTIR spectroscopy. The measured rate coefficient ratios $k(\text{NO}_3 + \text{butanal})/k(\text{NO}_3 + \text{propene}) = 1.1 \pm 0.1$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.42 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation). The rate coefficient ratio was independent of the presence or absence of O₂.
- NO₃ radicals were generated by the thermal dissociation of N₂O₅. Experiments were carried out in 1 atmosphere of air with measurements of butanal and methacrolein (the reference

compound) by GC. The measured rate coefficient ratio $k(\text{NO}_3 + \text{butanal})/k(\text{NO}_3 + \text{methacrolein}) = 3.38 \pm 0.15$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{methacrolein}) = 3.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

Preferred Values

$k = 1.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.7 \times 10^{-12} \exp(-1500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260-340 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the room temperature relative rate coefficients of D'Anna and Nielsen (1997), Ullerstam et al. (2000), D'Anna et al. (2001) and Papagni et al. (2001) and the absolute rate coefficients of Ullerstam et al. (2000) [measured in the presence of O_2] and Bossmeyer et al. (2006). The absolute rate coefficient measured at 298 K by Cabañas et al. (2001) is 20-40% higher than the other absolute and relative rate coefficients, possibly indicating the occurrence of secondary reactions. The two measurements of the temperature dependence (Ullerstam et al., 2000; Cabañas et al., 2001) disagree significantly, with the pre-exponential factor derived from the study of Cabañas et al. (2001) being within a factor of ~ 5 of gas kinetic. The preferred temperature dependence is that obtained from the study of Ullerstam et al. (2000), with a high uncertainty being assigned.

References

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