

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO₃_VOC25

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This data sheet updated: 10th December 2007 (with no revision of the preferred values).

NO₃ + (CH₃)₂C(OH)CH=CH₂ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$4.6 \times 10^{-14} \exp[-(400 \pm 35)/T]$	267-400	Rudich et al., 1996	F-A (a)
$(1.21 \pm 0.09) \times 10^{-14}$	298		
$(2.1 \pm 0.3) \times 10^{-14}$	294	Hallquist et al., 1996	DF-A
<i>Relative Rate Coefficients</i>			
$(1.55 \pm 0.55) \times 10^{-14}$	294	Hallquist et al., 1996	RR (b)
$(8.7 \pm 3.0) \times 10^{-15}$	298 ± 2	Fantechi et al., 1998a	RR (c)
$(1.0 \pm 0.2) \times 10^{-14}$	297 ± 2	Noda et al., 2002	RR (d)
$(1.1 \pm 0.1) \times 10^{-14}$	297 ± 2	Noda et al., 2002	RR (e)

Comments

- NO₃ radicals were generated by the thermal decomposition of N₂O₅ at 400 K in a flow system, and NO₃ radical concentrations were measured by visible tunable diode laser absorption at 661.9 nm.
- NO₃ radicals were generated by the thermal decomposition of N₂O₅ in N₂O₅-(CH₃)₂C(OH)CH=CH₂-propene (the reference compound)-diluent (not specified) mixtures at 1013 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and propene were measured by FTIR spectroscopy, and the measured rate coefficient ratio $k(\text{NO}_3 + 2\text{-methyl-3-buten-2-ol})/k(\text{NO}_3 + \text{propene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 294 K (IUPAC, current recommendation).
- NO₃ radicals were generated by the thermal decomposition of N₂O₅ in N₂O₅-(CH₃)₂C(OH)CH=CH₂-propene (the reference compound)-air mixtures at 987 ± 7 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and propene were measured by FTIR spectroscopy, and the measured rate coefficient ratio $k(\text{NO}_3 + 2\text{-methyl-3-buten-2-ol})/k(\text{NO}_3 + \text{propene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).
- NO₃ radicals were generated by the thermal decomposition of N₂O₅ in N₂O₅-(CH₃)₂C(OH)CH=CH₂-propene (the reference compound)-air (or N₂) mixtures at ~1.02 bar pressure. The concentrations of 2-methyl-3-buten-2-ol and propene were measured by FTIR spectroscopy, and the measured rate coefficient ratio $k(\text{NO}_3 + 2\text{-methyl-3-buten-2-ol})/k(\text{NO}_3 + \text{propene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation).
- NO₃ radicals were generated by the thermal decomposition of N₂O₅ in N₂O₅-(CH₃)₂C(OH)CH=CH₂-butanal (the reference compound)-air (or N₂) mixtures at 1.01 ± 0.01 bar pressure. The concentrations of 2-methyl-3-buten-2-ol and butanal were measured by collection onto solid phase microextraction fibers with GC analyses. The measured rate

coefficient ratio $k(\text{NO}_3 + 2\text{-methyl-3-buten-2-ol})/k(\text{NO}_3 + \text{butanal})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{butanal}) = 1.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation).

Preferred Values

$k = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 4.6 \times 10^{-14} \exp(-400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260-400 K.

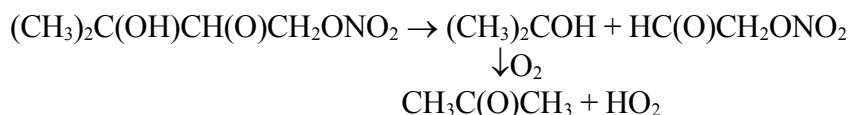
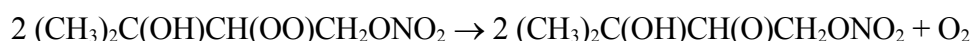
Reliability

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

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

At room temperature, the relative rate coefficients of Hallquist et al. (1996), Fantechi et al. (1998a) and Noda et al. (2002) are in agreement, within the combined error limits, with the absolute rate coefficient of Rudich et al. (1996). However, the absolute rate coefficient of Hallquist et al. (1996) is a factor of 1.7 higher than that of Rudich et al. (1996). The absolute data of Rudich et al. (1996) are the basis for the preferred values. The reaction proceeds by initial addition of NO_3 to the C=C bond (Fantechi et al., 1998b; Noda et al., 2000), forming (after addition of O_2) the peroxy radicals $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}_2\text{OO}$ and $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{OO})\text{CH}_2\text{ONO}_2$ [and mainly the $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{OO})\text{CH}_2\text{ONO}_2$ radical (see below)]. Reactions of these peroxy radicals with HO_2 radicals, organic peroxy radicals, NO , NO_2 , and NO_3 radicals will lead to the products observed in the atmosphere (Atkinson and Arey, 2003). Under laboratory conditions, the observed products at atmospheric pressure of air are acetone and $\text{O}_2\text{NOCH}_2\text{CHO}$, with measured molar yields of $68.7 \pm 7.1\%$ (Fantechi et al., 1998b) and $63 \pm 6\%$ (Noda et al., 2000) for acetone and $67 \pm 8\%$ for 2-nitrooxyacetaldehyde (Noda et al., 2000). These observed products presumably arise from self-reaction of the $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{OO})\text{CH}_2\text{ONO}_2$ peroxy radical, followed by decomposition of the resulting $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{O})\text{CH}_2\text{ONO}_2$ radical:



References

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