

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO₃_VOC8

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This data sheet updated: 12th December 2007 (with no revision of the preferred values).

NO₃ + CH₂=C(CH₃)CH=CH₂ (isoprene) → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(1.3 \pm 0.14) \times 10^{-12}$	298	Benter and Schindler, 1988	DF-MS
$3.03 \times 10^{-12} \exp[-(450 \pm 70)/T]$	251-381	Dlugokencky and Howard, 1989	F-LIF (a)
$(6.52 \pm 0.78) \times 10^{-13}$	297		
$(7.30 \pm 0.44) \times 10^{-13}$	298	Wille et al., 1991	DF-MS
$(8.26 \pm 0.60) \times 10^{-13}$	298	Wille et al., 1991; Lancar et al., 1991	DF-MS
$(1.07 \pm 0.20) \times 10^{-12}$	295 ± 2	Ellermann et al., 1992	PR-A (b)
$(7.3 \pm 0.2) \times 10^{-13}$	298 ± 2	Suh et al., 2001	F-CIMS (c)
<i>Relative Rate Coefficients</i>			
$(5.94 \pm 0.16) \times 10^{-13}$	295 ± 1	Atkinson et al., 1984	RR (d)
$(1.21 \pm 0.20) \times 10^{-12}$	298 ± 2	Barnes et al., 1990	RR (e)
$(6.86 \pm 0.55) \times 10^{-13}$	298	Berndt and Böge, 1997	RR (f)

Comments

- NO₃ radicals were generated by thermal decomposition of N₂O₅ in a flow system at total pressures of 1.0-1.1 Torr (1.3-1.5 mbar), and monitored by LIF.
- NO₃ radicals were generated by pulse radiolysis of SF₆-HNO₃-isoprene mixtures at 1 bar total pressure, and monitored by optical absorption at 662 nm.
- NO₃ radicals were generated by thermal decomposition of N₂O₅ in a flow system at total pressures of 5.1-6.0 Torr (6.8-8.0 mbar), and monitored by CIMS using the reaction NO₃ + SF₆⁻ → NO₃⁻ + SF₆.
- Relative rate method carried out at atmospheric pressure of air. NO₃ radicals were generated by thermal decomposition of N₂O₅. The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. Small corrections (2-4%) to the measured isoprene concentrations were made to take into account the gas-phase reaction of isoprene with NO₂ (Atkinson et al., 1984; Atkinson, 1997). The resulting rate coefficient ratio of $k(\text{NO}_3 + \text{isoprene})/k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 1.53 \pm 0.04$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 3.88 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (Atkinson, 1997).
- Relative rate method carried out at atmospheric pressure of synthetic air. NO₃ radicals were generated by thermal decomposition of N₂O₅. The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. No corrections for the reaction of isoprene with NO₂ were found to be necessary. The measured rate coefficient ratio of $k(\text{NO}_3 + \text{isoprene})/k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 3.1 \pm 0.5$ is placed on an absolute basis by use of a rate

coefficient of $k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 3.90 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 1997).

- (f) Relative rate method carried out in a flow system at a total pressure of 6.8 mbar (5.1 Torr) of N_2 . NO_3 radicals were generated by thermal decomposition of N_2O_5 . The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{NO}_3 + \textit{isoprene})/k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 1.76 \pm 0.14$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 3.90 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 1997).

Preferred Values

$k = 7.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.15 \times 10^{-12} \exp(-450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250-390 K.

Reliability

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

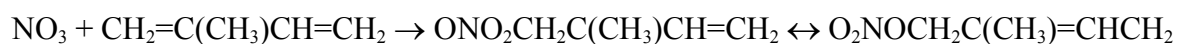
$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The measured room temperature rate coefficients range over a factor of 2.2, irrespective of whether absolute or relative rate methods were used. The study of Wille et al. (1991) is stated (Wille et al., 1991) to supersede the earlier study of Benter and Schindler (1988) carried out over a more restricted range of conditions and in which heterogeneous reactions between isoprene and F_2 could have occurred (Wille et al., 1991). The only temperature dependent measurement of the kinetics of this reaction is from Dlugokencky and Howard (1989). The preferred 298 K rate coefficient is an average of the room temperature absolute and relative rate coefficients of Dlugokencky and Howard (1989), Wille et al. (1991), Lancar et al. (1991), Suh et al. (2001), Atkinson et al. (1984) and Berndt and Böge (1997), which are in reasonably good agreement. The temperature dependence of Dlugokencky and Howard (1989) is accepted, and the pre-exponential factor is calculated from the 298 K preferred rate coefficient and the temperature dependence.

The reaction proceeds by initial addition of the NO_3 radical to the carbon-carbon double bonds (Atkinson, 1997). At low pressures the products are NO_2 plus an oxirane (Atkinson, 1997). The formation yield of the oxirane decreases with increasing total pressure and with increasing O_2 concentration (Atkinson, 1997), with oxirane formation at atmospheric pressure of air being of no importance (Skov et al., 1994; Atkinson, 1997). Using *in situ* FTIR spectroscopy, Skov et al. (1992) reported that the products formed at atmospheric pressure of air are $\text{O}_2\text{NOCH}_2\text{C}(\text{CH}_3)=\text{CHCHO}$ as the major product, and with $\text{O}_2\text{NOCH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CHO}$, $\text{O}_2\text{NOCH}_2\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$, $\text{O}_2\text{NOCH}_2\text{CH}(\text{OH})\text{C}(\text{CH}_3)=\text{CH}_2$ and $\text{O}_2\text{NOCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OH}$ as minor products. Using atmospheric pressure ionization tandem mass spectrometry Kwok et al. (1996) observed $\text{O}_2\text{NOCH}_2\text{C}(\text{CH}_3)=\text{CHCHO}$ (and isomers), $\text{O}_2\text{NOCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OH}$ (and isomers), $\text{O}_2\text{NOCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OOH}$ (and isomers), and $\text{HOCH}_2\text{C}(\text{CH}_3)=\text{CHCHO}$ (and isomers) as products of the reaction (again at atmospheric pressure of air). Kwok et al. (1996) also observed the formation of methacrolein and methyl vinyl ketone, with measured formation yields of each of these α,β -unsaturated carbonyls being $3.5 \pm 1.4\%$.

The FTIR study of Skov et al. (1992) indicates that the NO_3 radical adds dominantly to the 1- and 4-positions, in a 3.5:1 ratio. At atmospheric pressure of air, the reaction then proceeds mainly by,



followed by addition of O₂ to form the corresponding peroxy radicals ONO₂CH₂C(OO)(CH₃)CH=CH₂ and O₂NOCH₂C(CH₃)=CHCH₂OO. These peroxy radicals then react with NO, NO₂, HO₂ and organic peroxy radicals (Atkinson, 1997), depending on the concentrations of these species.

References

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