

IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet NO3_VOC14

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

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
(1.3 ± 0.14) × 10 ⁻¹²	298	Benter and Schindler, 1988 ¹	DF-MS
3.03 × 10 ⁻¹² exp[-(450 ± 70)/T]	251-381	Dlugokencky and Howard, 1989 ²	F-LIF (a)
(6.52 ± 0.78) × 10 ⁻¹³	297		
(7.30 ± 0.44) × 10 ⁻¹³	298	Wille <i>et al.</i> , 1991 ³	DF-MS
(8.26 ± 0.60) × 10 ⁻¹³	298	Wille <i>et al.</i> , 1991 ³ ; Lancar <i>et al.</i> , 1991 ⁴	DF-MS
(1.07 ± 0.20) × 10 ⁻¹²	295 ± 2	Ellermann, Nielsen, and Skov, 1992 ⁵	PR-A (b)
(7.3 ± 0.2) × 10 ⁻¹³	298 ± 2	Suh, Lei, and Zhang, 2001 ⁶	F-CIMS (c)
<i>Relative Rate Coefficients</i>			
(5.94 ± 0.16) × 10 ⁻¹³	295 ± 1	Atkinson <i>et al.</i> , 1984 ⁷	RR (d)
(1.21 ± 0.20) × 10 ⁻¹²	298 ± 2	Barnes <i>et al.</i> , 1990 ⁸	RR (e)
(6.86 ± 0.55) × 10 ⁻¹³	298	Berndt and Böge, 1997 ⁹	RR (f)

Comments

- (a) 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.
- (b) 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.
- (c) 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.
- (d) 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.^{7,10} 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.¹⁰
- (e) 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 $k(\text{NO}_3 + \text{isoprene})/k(\text{NO}_3 + \text{trans-2-butene}) = 3.1 \pm 0.5$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{trans-2-butene}) = 3.90 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.¹⁰

- (f) Relative rate method carried out in a flow system at a total pressure of 6.8 mbar (5.1 Torr) of N₂. NO₃ radicals were generated by thermal decomposition of N₂O₅. The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{NO}_3 + \text{isoprene})/k(\text{NO}_3 + \text{trans-2-butene}) = 1.76 \pm 0.14$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{trans-2-butene}) = 3.90 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.¹⁰

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.

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

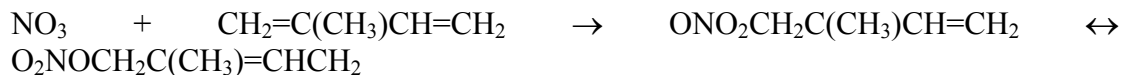
Comments on Preferred Values

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.*³ is stated³ to supersede the earlier study of Benter and Schindler¹ carried out over a more restricted range of conditions (and in which heterogeneous reactions between isoprene and F₂ could have occurred³). The only temperature dependent measurements of the kinetics of this reaction are from Dlugokencky and Howard.² The preferred 298 K rate coefficient is an average of the room temperature absolute and relative rate coefficients of Dlugokencky and Howard,² Wille *et al.*,³ Lancar *et al.*,⁴ Suh *et al.*,⁶ Atkinson *et al.*⁷ and Berndt and Böge,⁹ which are in reasonably good agreement. The temperature dependence of Dlugokencky and Howard² 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 NO₃ radical to the carbon-carbon double bonds.¹⁰ At low pressures the products are NO₂ plus an oxirane.¹⁰ The formation yield of the oxirane decreases with increasing total pressure and with increasing O₂ concentration,¹⁰ with oxirane formation at atmospheric pressure of air being of no importance.^{10,11} Using *in situ* FTIR spectroscopy, Skov *et al.*¹² reported that the products formed at atmospheric pressure of air are O₂NOCH₂C(CH₃)=CHCHO as the major product, and with O₂NOCH₂CH=C(CH₃)CHO, O₂NOCH₂C(O)C(CH₃)=CH₂, O₂NOCH₂CH(OH)C(CH₃)=CH₂ and O₂NOCH₂C(CH₃)=CHCH₂OH as minor products. Using atmospheric pressure ionization tandem mass spectrometry Kwok *et al.*¹³ observed O₂NOCH₂C(CH₃)=CHCHO (and isomers), O₂NOCH₂C(CH₃)=CHCH₂OH (and isomers), O₂NOCH₂C(CH₃)=CHCH₂OOH (and isomers), and HOCH₂C(CH₃)=CHCHO (and isomers) as products of the reaction (again at atmospheric pressure of air). Kwok *et al.*¹³ 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.*¹² 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 O_2 to form the corresponding peroxy radicals $\text{ONO}_2\text{CH}_2\text{C}(\text{OO})(\text{CH}_3)\text{CH}=\text{CH}_2$ and $\text{O}_2\text{NOCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OO}$. These peroxy radicals then react with NO , NO_2 , HO_2 and organic peroxy radicals,¹⁰ depending on the concentrations of these species.

References

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