

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

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This datasheet last evaluated: July 2015; last change in preferred values: July 2015.

NO₃ + 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) |
| $(5.33 \pm 0.21) \times 10^{-13}$ | 296 ± 2 | Stabel et al., 2004 | RR (g) |
| $(7.0 \pm 0.6) \times 10^{-13}$ | | | RR(h) |
| $(6.13 \pm 0.12) \times 10^{-13}$ | 295 ± 2 | Zhao et al., 2011 | RR (i) |

Isoprene is 2-methyl-1,3-butadiene, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$

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 $\text{NO}_3 + \text{SF}_6^- \rightarrow \text{NO}_3^- + \text{SF}_6$.
- 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 $k(\text{NO}_3 + \text{isoprene})/k(\text{NO}_3 + \text{trans-2-butene}) = 1.53 \pm 0.04$ 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).

- (e) Relative rate method carried out at atmospheric pressure of synthetic air. 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. No corrections for the reaction of isoprene with NO_2 were found to be necessary. The measured rate coefficient ratio of $k(\text{NO}_3 + \textit{isoprene})/k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 3.1 \pm 0.5$ 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).
- (g) Relative rate method carried out at atmospheric pressure of synthetic air or N_2 . The temperature was reported as room temperature which we assume to be $(296 \pm 2) \text{ K}$. 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 $k(\text{NO}_3 + \textit{isoprene})/k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 1.367 \pm 0.055$ 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).
- (h) As comment (g) but using butene-1-ol as reference compound and with both GC and FTIR determination of concentrations. The measured, average, rate coefficient ratio of $k(\text{NO}_3 + \textit{isoprene})/k(\text{NO}_3 + \textit{butene}\text{-1-ol}) = 1.78 \pm 0.13$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \textit{butene}\text{-1-ol}) = (3.94 \pm 0.18) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature K. This value of $k(\text{NO}_3 + \textit{butene}\text{-1-ol})$ was derived from the rate constant ratio $k(\text{NO}_3 + \textit{butene}\text{-1-ol})/k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 1.011 \pm 0.0047$ (Noda et al., 2002).
- (i) Relative rate method carried out in a flow system at atmospheric pressure N_2 or synthetic air. NO_3 radicals (3×10^{10} to $2 \times 10^{12} \text{ molecule cm}^{-3}$) were generated by thermal decomposition of N_2O_5 . The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by CIMS. The measured rate coefficient ratio of $k(\text{NO}_3 + \textit{isoprene})/k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 1.58 \pm 0.03$ 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).

Preferred Values

$k = 6.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.95 \times 10^{-12} \exp(-450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250-390 K.

Reliability

$\Delta \log k = \pm 0.15$ 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. The study of Wille et al. (1991) is stated to supersede the earlier study of Benter and Schindler (1988). The most recent experiments indicate that the values at the lower end of the range measured are more reliable and 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), Suh et al. (2001), Atkinson et al. (1984), Berndt and Böge (1997), Stabel et al., (2004) and Zhao et al (2011).

The only temperature dependent measurement of the kinetics of this reaction is from Dlugokencky and Howard (1989). Their temperature dependence ($-450/T$) is accepted with the pre-exponential factor recalculated to match the preferred rate coefficient at 298 K.

The mechanism of the reaction has been elucidated in a series of studies that have measured end-products (Jay and Stieglitz., 1989; Skov et al. 1992; Kwok et al., 1996; Berndt and Böge 1997; Ng et al., 2008; Perring et al., 2009; Rollins et al., 2009; Kwan et al., 2012), the main one being the C₅-nitrooxycarbonyl, 4-nitrooxy-3-methyl-2-butanal.

The molar yield of organic nitrate relative to isoprene reacted has been determined to be between ~ 60 and 90 % (Barnes et al., 1992; Berndt and Böge, 1997; Perring et al., 2009; Kwan et al., 2012; Schwantes et al., 2015). The molar yield of organic nitrate relative to NO₃ reacted is also large with values between ~50 and 95 % reported (Berndt and Böge, 1997; Perring et al., 2009; Rollins et al., 2009; Kwan et al., 2012). The variability in the nitrate yields reflects use of different experimental conditions which influences the fate of the peroxy radicals formed (see below).

The reaction proceeds via addition of NO₃ to a double bond, forming 4 distinct nitrooxyalkyl radicals. Of the four potential sites of NO₃ addition, the 1- and 4-positions are most important. The ratio of the addition of NO₃ to these two positions has been experimentally determined to be 3.5:1 (Skov et al., 1992, determined via isotopic labelling of isoprene), between 5.1:1 and 7.4:1 (Berndt and Böge., 1997, derived via product analysis following NO addition) and 7(±1):1 (Schwantes et al., 2015, derived via product analysis when HO₂ was added) in favour of position 1. A value of (5.5 ± 2):1 is preferred, which covers the spread in the experimental data and is consistent with a theoretical value of 5.5:1 (Suh et al., 2001).

In air, the delocalised nitrooxyalkyl radicals formed from the C₁ addition adds O₂ to the 2 (β) or 4 (δ) positions to form the corresponding peroxy radicals ONO₂CH₂C(OO)(CH₃)CH=CH₂ and O₂NOCH₂C(CH₃)=CHCH₂OO. Experimental (Schwantes et al., 2015) and theoretical work (Zhao and Zhang, 2002) suggests that the δ-addition of O₂ is favoured so that (following equilibration) the dominant RO₂ would be O₂NOCH₂C(CH₃)=CHCH₂OO, the result of the 1,4 addition of NO₃ and O₂ to isoprene. These peroxy radicals (RO₂) can react with HO₂ to form C₅-nitrooxyhydroperoxides, with RO₂ to form C₅-nitrooxycarbonyl and C₅-hydroxynitrate and also C₁₀-nitrooxyperoxide (ROOR), with NO, RO₂ or NO₃ to form an alkoxy radical (RO) that can react to form the C₅-nitrooxycarbonyl (via reaction with O₂) or a C₅-hydroxycarbonyl (via elimination of NO₂). Nitrate-peroxynitrates, formed from RO₂ + NO₂ have been observed but are unstable and decay to carbonyl species (Barnes et al., 1992; Skov et al., 1992). The final products are dependent on experimental conditions including the relative concentrations of NO₃ and isoprene, the lifetime of the peroxy radicals and possibly the temperature, all of which may influence the distribution of the 6 possible RO₂ radicals.

Kwan et al. (2012) provide approximate branching ratios for the three potential self-reaction types of RO₂ to form R'CHO + ROH (59-77 %), 2 RO (19-38 %) and ROOR (3-4 %). Schwantes et al., (2015) also indicate that the rate constants for the RO₂ self-reactions are strongly dependent on the isomer. The dominant, 1,4 isomer is reported to have a self-reaction rate constant of $\sim 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ though Schwantes et al suggest that the presence of hydroxymethyl peroxy radicals in their system by bias this result somewhat.

Schwantes et al. (2015) show that that, on average ~ 75-78 % of the RO₂ + HO₂ reaction results in nitrooxyhydroperoxide formation, with 22 % forming methylvinylketone + OH + HCHO + NO₂ and the rest methacrolein + OH + HCHO + NO₂. The 1,4 and 4,1 isomers of RO₂ were found to yield only the nitrooxyhydroperoxide, with the OH coming from the β isomers (1,2 and 4,3). Large average OH yields (38-58%) from RO₂ + HO₂ were also found by Kwan et al.,

(2012). Though these experiments were carried out under less favourable conditions to study the products of $\text{RO}_2 + \text{HO}_2$.

The reaction of RO_2 with NO_3 is assumed, via analogy with smaller RO_2 to form the RO radical.

Non nitrated products are methacrolein, methyl vinyl ketone and 3-methylfuran. Kwok et al. (1996) report methacrolein and methyl vinyl ketone yields of 3.5 ± 1.4 % for both. This is consistent with the sum of 10 % reported by Perring et al (2009). In the presence of NO, the $\text{RO}_2 + \text{NO}$ pathway dominates and the yield of methyl vinyl ketone has been derived as 0.51 with some 3-methylfuran (0.17-0.18) and methacrolein (0.07 to 0.10) (Berndt and Böge, 1992).

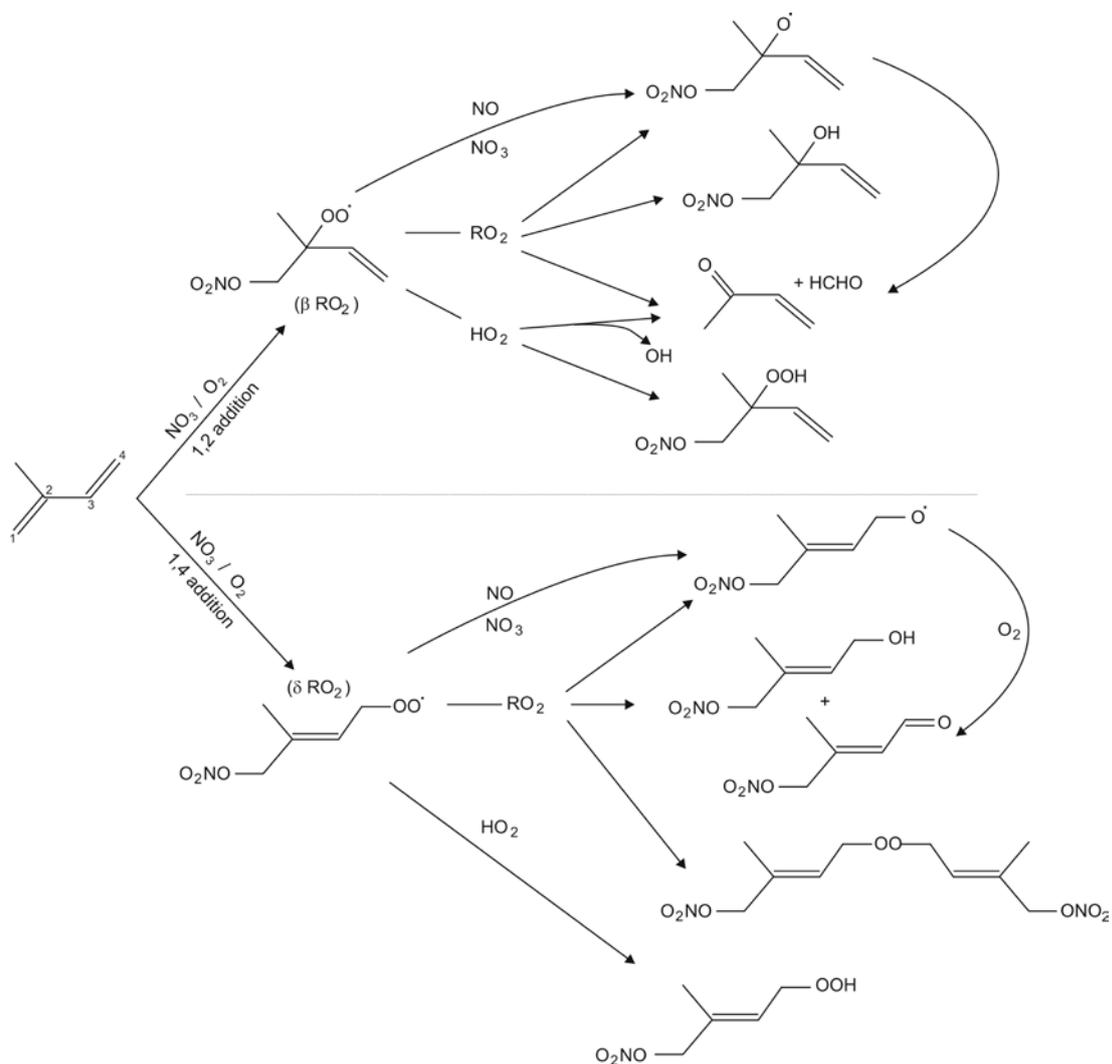
A reaction mechanism (adapted from Scheme 1 of Schwantes et al., 2015), showing the pathways to products (via HO_2 , RO_2 , NO and NO_3 reactions) from the most important δ and β RO_2 isomers (1,4 and 1,2) is displayed below.

Secondary organic aerosol (SOA, with mass yields of between ~4 and 24 % per isoprene reacted) has been observed to result from the NO_3 induced oxidation of isoprene in air (Ng et al., 2008; Rollins, 2009). SOA arises through the formation of low volatility products such as ROOR or dinitrates which stem from secondary, NO_3 induced oxidation of the first generation nitrates discussed above.

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Partial degradation scheme for isoprene following initial oxidation with NO_3 . Only stable, organic end products are shown. The likely reaction pathways of the dominant δ and β peroxy radicals (RO_2) formed in the 1,4 and 1,2 addition of NO_3 / O_2 are shown.