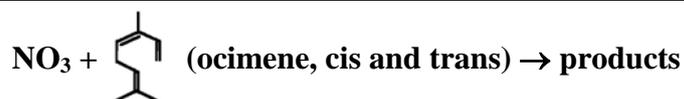


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO₃_VOC39

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This data sheet last evaluated: June 2013; last change in preferred values: June 2013.



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
$(2.23 \pm 0.06) \times 10^{-11}$	294	Atkinson et al., 1985	RR (a)
Ocimene is 3,7-dimethyl-1,3,6-octatriene.			

Comments

- (a) 4000 L Teflon chamber at 294 K and 980 mbar (735 Torr) of air. NO₃ was generated by the thermal decomposition of N₂O₅. Ocimene and 2-methyl-2-butene were monitored by GC. Correction made to the ocimene loss rate due to reaction with NO₂ was < 12 %. The rate constant ratio, $k(\text{NO}_3 + \text{ocimene}) / k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 2.38 \pm 0.06$ is placed on an absolute basis by $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson and Arey, 2003). The rate constants for the cis and trans-isomers of ocimene were indistinguishable within experimental uncertainty (8%).

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.2×10^{-11}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the room temperature rate coefficient is based on the single study of Atkinson et al. (1985). The error limits are expanded to reflect the necessity to correct for removal of ocimene by reaction with NO₂ and because the results have not been confirmed. There are no product studies of this reaction, though the large rate constant indicates that the reaction proceeds mainly via addition of NO₃ across a double bond to form a chemically activated nitrooxyalkyl radical. At pressures found in the troposphere this adduct will undergo collisional stabilization prior to reaction with O₂ to form a nitrooxyalkyl peroxy radical or

decompose to release NO₂. At atmospheric pressure the formation of the peroxy radical will generally dominate.

References

Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N.: *Env. Sci. Tech.*, 19, 159-163, 1985.

Atkinson, R., and Arey, J.: *Chem. Rev.*, 103, 4605-4638, 2003.