Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC39

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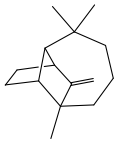
O_3 +  **(longifolene[a]) → products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$< 7 \times 10^{-18}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(c)
$< 5 \times 10^{-19}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(d)

Comments

(a) (1R,2S,7S,9S)-3,3,7-trimethyl-8-methylenetricyclo[5.4.0.0^{2,9}]undecane.

(b) The concentrations of longifolene and *cis*-but-2-ene or propene (the reference compounds), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in 6400–6900 L all Teflon chambers at 740 Torr (990 mbar) pressure of purified air in the presence of O_3. The measured rate coefficient ratios, $k(O_3$ + longifolene/$k(O_3$ + *cis*-but-2-ene) and $k(O_3$ + longifolene/$k(O_3$ + propene) < 0.05, are placed on an absolute basis using $k(O_3$ + *cis*-but-2-ene) = 1.23×10^{-16} cm^3 molecule^{-1} s^{-1} and $k(O_3$ + propene) = 9.59×10^{-18} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation) at 296 K.

(c) Relative to *cis*-but-2-ene.

(d) Relative to propene.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	$< 5 \times 10^{-19}$	298

Comments on Preferred Values

The more stringent upper limit for the value of k reported in the study of Shu and Atkinson (1994) is adopted for the preferred value. This is based on no quantifiable decay of longifolene occurring in mixtures with O_3 and propene (with cyclohexane to scavenge HO radicals), for up to 75 % decay in the propene concentration. The low value of k compared to those for other terpenes possessing methylene groups (e.g. β-pinene and sabinene) is most likely due to steric hindrance resulting from the bridged ring structure.

References

Shu, Y. and Atkinson, R.: Int. J. Chem. Kinet., 26, 1193, 1994.