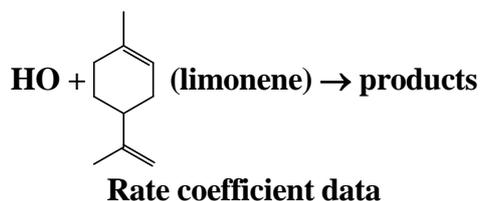


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC100

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This datasheet last evaluated: December 2017; last change in preferred values: December 2017



$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$4.59 \times 10^{-11} \exp[(382 \pm 154)/T]$	300-360	Braure et al., 2014	DF-MS (a)
1.65×10^{-10}	300		
<i>Relative Rate Coefficients</i>			
$(1.45 \pm 0.22) \times 10^{-10}$	305 ± 2	Winer et al., 1976	RR (b)
$(1.66 \pm 0.50) \times 10^{-10}$	294 ± 1	Atkinson et al., 1986	RR (c)
$4.20 \times 10^{-11} \exp[(401 \pm 43)/T]$	295-364	Gill and Hites, 2002	RR (d)
$(1.61 \pm 0.31) \times 10^{-10}$	298		
$2.53 \times 10^{-11} \exp[(569 \pm 56)/T]$	220-355	Braure et al., 2014	DF-MS (a)
1.70×10^{-10}	298*		

limonene is 4-isopropenyl-1-methyl-cyclohexene

Comments

- (a) Both absolute and relative rate determinations reported, carried out in 1 Torr (1.3 mbar) of He. Absolute rate coefficients determined mainly from observed decay of HO concentration in excess limonene, but with some experiments monitoring the decay of limonene concentration in excess HO. k was also reported to be independent of pressure over the range 0.5-5 Torr (0.7-6.7 mbar). Relative rate determinations carried out using either the HO + CH₃SSCH₃ reaction or the HO + Br₂ reaction as a reference, with the latter monitored using the formation of the product HOBr. The measured rate coefficient ratios $k(\text{HO} + \text{limonene})/k(\text{HO} + \text{CH}_3\text{SSCH}_3)$ and $k(\text{HO} + \text{limonene})/k(\text{HO} + \text{Br}_2)$ are placed on an absolute basis using $k(\text{HO} + \text{CH}_3\text{SSCH}_3) = 7.0 \times 10^{-11} \exp(350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + \text{Br}_2) = 1.9 \times 10^{-11} \exp(240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC current recommendations). The authors preferred to report a rate expression based on a combined analysis of all data. Applying the above reference rate coefficients, this results in the slightly adjusted expression, $k = 2.8 \times 10^{-11} \exp(543/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220-360 K, which is used here to represent their data. Almost identical temperature-dependent rate coefficients were also reported for the DO + limonene reaction, with the branching ratio for H atom abstraction described by $(0.07 \pm 0.03) \exp((460 \pm 140)/T)$ over the temperature range 253-355K, based on monitoring the formation of HDO.
- (b) HO radicals were generated by the photolysis of NO_x - organic - air mixtures in a 5870 L chamber at ~1 bar pressure. The concentrations of limonene and 2-methylpropene (the reference compound) were analyzed by GC. The measured rate coefficient ratio $k(\text{HO} + \text{limonene})/k(\text{HO} + 2\text{-methylpropene})$ is placed on an absolute basis using $k(\text{HO} + 2\text{-methylpropene}) = 4.92 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 305 K (IUPAC current recommendation).
- (c) HO radicals were generated by the photolysis of CH₃ONO in air at wavelengths >300 nm in a

6400 L Teflon chamber at ~980 mbar pressure. The concentrations of limonene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC during UV irradiation of CH₃ONO - NO - limonene - 2,3-dimethyl-2-butene - air mixtures. The measured rate coefficient ratio $k(\text{HO} + \text{limonene})/k(\text{HO} + 2,3\text{-dimethyl-2-butene}) = 1.51 \pm 0.04$ is placed on an absolute basis using $k(\text{HO} + 2,3\text{-dimethyl-2-butene}) = 1.10 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).

- (d) HO radicals were generated by the photolysis of H₂O₂ in helium diluent in a 192 cm³ volume quartz vessel. The concentrations of limonene and 1-butene, 2-methylpropene or *trans*-2-butene (the reference compounds) were analyzed by MS. The measured rate coefficient ratios $k(\text{HO} + \text{limonene})/k(\text{HO} + 1\text{-butene})$, $k(\text{HO} + \text{limonene})/k(\text{HO} + 2\text{-methylpropene})$ and $k(\text{HO} + \text{limonene})/k(\text{HO} + \textit{trans}\text{-2-butene})$ are placed on an absolute basis using $k(\text{HO} + 1\text{-butene}) = 6.6 \times 10^{-12} \exp(465/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k(\text{HO} + 2\text{-methylpropene}) = 9.4 \times 10^{-12} \exp(505/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + \textit{trans}\text{-2-butene}) = 1.0 \times 10^{-11} \exp(553/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC current recommendations).

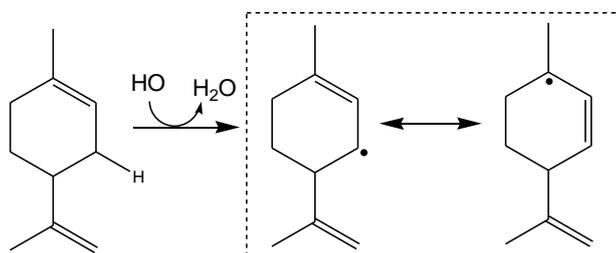
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.65×10^{-10}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.41 \times 10^{-11} \exp(470/T)$	220-360
<i>Reliability</i>		
$\Delta \log k$	± 0.05	298
$\Delta E/R$	± 150	

Comments on Preferred Values

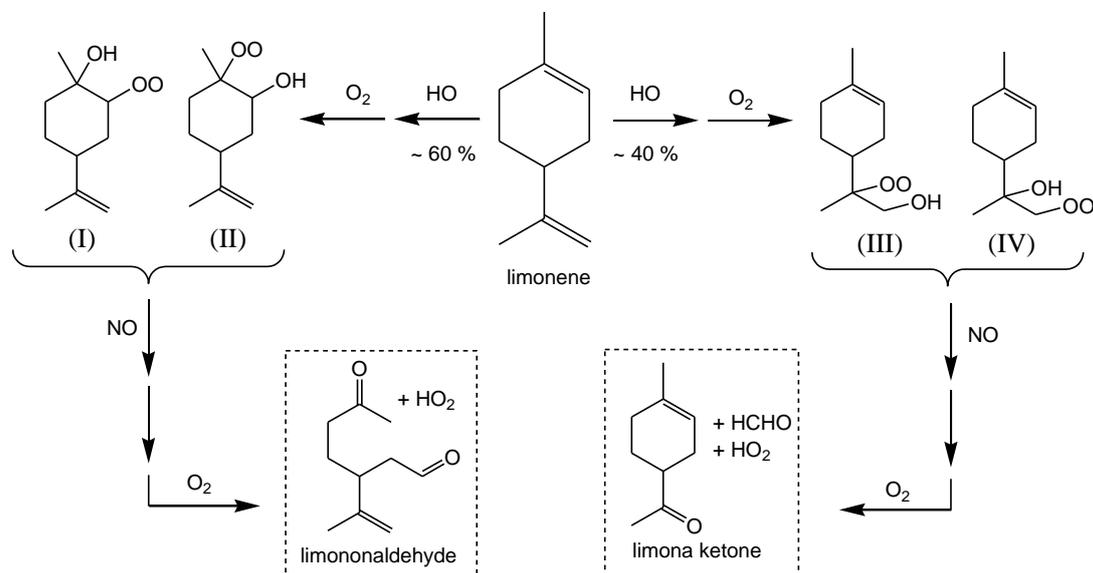
The preferred value of E/R is a rounded average of the values of Gill and Hites (2002) and Braure et al. (2014), with the latter based on the composite analysis of all their data (see comment (a)). The 298 K preferred value of k is the average of the room temperature values reported by Atkinson et al. (1986), corrected to 298 K using the preferred temperature dependence, Gill and Hites (2002) and Braure et al. (2014), based on the composite analysis of all their data (see comment (a)), which are in good agreement. The determination of Winer et al. (1974) is about 10 % lower than the preferred value, but within the assigned uncertainty bounds. The pre-exponential factor is adjusted to fit the 298 K preferred value.

H-atom abstraction has been reported to account for about 30 % of the reaction of HO (or DO) with limonene at 298 K (Rio et al., 2010; Braure et al., 2014). Rio et al. (2010) derived their value from analysis of the time-dependence of composite product peroxy radical absorptions (UV absorption) in air at atmospheric pressure, and from observation of product radical fragments (MS) at low pressure in the absence of O₂. Braure et al. (2014) derived their value from formation of HDO from the reaction of DO with limonene. They also observed an unexpected negative temperature dependence in the branching ratio (see comment (a)), suggesting a contribution of H-atom abstraction of over 40% at 250 K. A significant contribution of H-atom abstraction is expected to be facilitated by formation of resonant product radicals, following abstraction at five of the six available (saturated carbon) sites, e.g.:



However, theoretical (Dash and Rajakumar, 2015) and structure activity methods (Vereecken and Peeters, 2001), predict a much lower contribution of about 3-17 % from H-atom abstraction at 298 K, and a positive temperature dependence. Confirmatory experimental and theoretical studies would therefore be valuable.

HO addition is expected to occur significantly at both the endocyclic and exocyclic double bonds in limonene, and the schematic below illustrates some established features of the subsequent chemistry in air in the presence of NO_x .



The hydroxy-substituted peroxy radicals, (I) and (II), are formed from sequential addition of HO and O_2 to the endocyclic bond, and (III) and (IV) are formed from addition to the exocyclic bond; with the approximate addition contributions shown based on structure activity methods (Peeters et al., 2007). The subsequent chemistry, propagated by the reactions of intermediate peroxy radicals with NO, forms a number of carbonyl end products (as shown in boxes). The chemistry of (I) and (II) generates limononaldehyde (3-isopropenyl-6-oxo-heptanal), for which yields of 28 % and 29 ± 6 % in the presence of NO_x have been reported by Arey et al. (1990) and Hakola et al. (1994) respectively. The chemistry of (III) and (IV) generates limona ketone (4-acetyl-1-methyl-cyclohexene), for which the reported yields are 17.4 ± 2.8 % (Arey et al., 1990) and 20 ± 3 % (Hakola et al., 1994). Its co-product, formaldehyde, has been reported to be formed with a yield of 43 ± 5 % in photo-oxidation experiments (Lee et al., 2006), although limonene was partially reacting with O_3 under their experimental conditions. The reactions of all the peroxy radicals with NO also partially form the corresponding hydroxy-nitrate products (not shown in the schematic), which have been reported to be formed with a collective yield of about 23% by Ruppert et al. (1999).

Other reactions of the intermediate peroxy radicals can compete with reaction with NO under atmospheric conditions, and in experimental studies with low NO_x levels. These include bimolecular reactions with HO_2 and organic peroxy radicals, which can have propagating channels (leading to lower yields of the same end products discussed above) and terminating channels generating hydroxy-hydroperoxide, hydroxy-carbonyl and dihydroxy products.

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