

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC8

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HO + CH₂=C(CH₃)CH=CH₂ (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>			
$2.36 \times 10^{-11} \exp[(409 \pm 28)/T]$	299-422	Kleindienst et al., 1982	FP-RF
$(9.26 \pm 1.5) \times 10^{-11}$	299		
$9.7 \times 10^{-11} (T/298)^{-1.36}$	249-348	Siese et al., 1994	FP-RF
9.7×10^{-11}	298		
$(1.10 \pm 0.05) \times 10^{-10}$	298	Stevens et al., 1999	DF-LIF
$2.70 \times 10^{-11} \exp[(336 \pm 74)/T]$	251-342	Campuzano-Jost et al., 2000	PLP-LIF (a)
$(8.56 \pm 0.26) \times 10^{-11}$	297		
$(1.10 \pm 0.04) \times 10^{-10}$	300	Chuong and Stevens, 2000	DF-LIF (b)
$(9.6 \pm 0.5) \times 10^{-11}$	295	McGivern et al., 2000	PLP-LIF (c)
$(1.01 \pm 0.08) \times 10^{-10}$	298 ± 2	Zhang et al., 2000	DF-CIMS (d)
9.1×10^{-11}	298 ± 2	Zhang et al., 2001	DF-CIMS (e)
$(1.08 \pm 0.05) \times 10^{-10}$	300	Chuong and Stevens, 2002	DF-LIF (f)
$2.68 \times 10^{-11} \exp[(348 \pm 136)/T]$	251-342	Campuzano-Jost et al., 2004	PLP-LIF (g)
$(8.47 \pm 0.59) \times 10^{-11}$	297		
$(1.00 \pm 0.15) \times 10^{-10}$	293	Spangenberg et al., 2004	PLP-LIF (h)
$(1.00 \pm 0.12) \times 10^{-10}$	294 ± 1.1	Karl et al., 2004	(i)
$(1.02 \pm 0.09) \times 10^{-10}$	295 ± 1	Poppe et al., 2007	(i)
$(1.12 \pm 0.07) \times 10^{-10}$	296 ± 2		
$(1.07 \pm 0.08) \times 10^{-10}$	290.5 ± 2.5		
$(9.7 \pm 0.8) \times 10^{-11}$	291 ± 2		
$(9.9 \pm 0.8) \times 10^{-11}$	290 ± 1		
$1.93 \times 10^{-11} \exp[(466 \pm 12)/T]$	241-356	Dillon et al., 2017	PLP-LIF (j)
$(9.3 \pm 0.4) \times 10^{-11}$	297		
$1.80 \times 10^{-11} \exp[(522 \pm 28)/T]$	298-794	Medeiros et al., 2018	PLP-LIF (k),(l)
$(9.90 \pm 0.09) \times 10^{-11}$	298		(k),(l)
$(1.06 \pm 0.02) \times 10^{-10}$	298		(k),(m)
$(1.04 \pm 0.02) \times 10^{-10}$	298		(k),(n)
<i>Relative Rate Coefficients</i>			
7.2×10^{-11}	300	Cox et al., 1980	RR (o)
$(1.08 \pm 0.05) \times 10^{-10}$	299 ± 2	Atkinson et al., 1982	RR (p)
$(9.90 \pm 0.27) \times 10^{-11}$	297 ± 2	Ohta, 1983	RR (q)
$(1.10 \pm 0.04) \times 10^{-10}$	295 ± 1	Atkinson and Aschmann, 1984	RR (r)
$(1.09 \pm 0.02) \times 10^{-10}$	297 ± 1	Edney et al., 1986	RR (s)
$(1.11 \pm 0.23) \times 10^{-10}$	298	McQuaid et al., 2002	RR (t)
$2.54 \times 10^{-11} \exp[(409 \pm 42)/T]$	298-363	Gill and Hites, 2002	RR (u)
$(1.00 \pm 0.05) \times 10^{-10}$	298		

$(1.06 \pm 0.04) \times 10^{-10}$	298 ± 2	Iida et al., 2002	RR (v)
$2.33 \times 10^{-11} \exp[(444 \pm 27)/T]$	240-340	Singh and Li, 2007	RR (w)
$(1.07 \pm 0.03) \times 10^{-10}$	298		RR (w,x)
$(1.11 \pm 0.02) \times 10^{-10}$	298		RR (w,y)
$3.97 \times 10^{-11} \exp[(249 \pm 20)/T]$	323-413	Hites and Turner, 2009	RR (u)

Comments

- (a) Rate coefficients for the reactions of HO radicals with isoprene-d₆ and DO radicals with isoprene were also measured at 297 K, these being $(8.31 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(8.27 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively.
- (b) Carried out at total pressures of 2-6 Torr (2.7-8.0 mbar) of helium diluent. No pressure dependence of the rate coefficient was observed at 300 K. However, at higher temperatures (321-423 K) the rate coefficient increased with increasing total pressure, with the effect being more pronounced at higher temperature.
- (c) Carried out at total pressures of 0.5-20 Torr (0.7-27 mbar) of argon diluent. The rate coefficient was observed to be pressure dependent below 10 Torr total pressure; the value cited in the table is that measured at 20 Torr total pressure.
- (d) Carried out at total pressures of 72.7-112.7 Torr (97-150 mbar) of N₂ diluent. The measured rate coefficient was independent of pressure over this range.
- (e) Based on a very limited kinetic study carried out at a total pressure of 1.9 Torr (2.5 mbar) of helium diluent (the focus of the study was on formation of HO-isoprene adducts and their subsequent reactions).
- (f) Carried out at total pressures of argon diluent of 100 Torr (133 mbar) and 150 Torr (200 mbar). The measured rate coefficient was independent of total pressure over this range.
- (g) Rate coefficients for HO + isoprene-d₆ and DO + isoprene were also measured at 297 K, with values of $(8.27 \pm 0.17) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(8.43 \pm 0.18) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Isoprene and isoprene-d₆ concentrations in the gas flow stream were measured before and after the reaction cell by UV absorption at 228.9 nm. The data from this study are in excellent agreement with those previously reported by Campuzano-Jost et al. (2000) at the same temperatures, and are assumed to supersede the earlier study.
- (h) Rate coefficients were also measured at 58, 71, 84, 104 and 114 K, with the rate coefficients of $(7.8 \pm 1.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $(1.14 \pm 0.17) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $(9.8 \pm 1.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $(1.88 \pm 0.28) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(1.68 \pm 0.25) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively.
- (i) Carried out in a large volume (270 m³) chamber. HO radicals were measured by LIF and isoprene was measured by GC (Karl et al., 2004; Poppe et al., 2007) or by proton-transfer-reaction mass spectrometry (Poppe et al., 2007) during irradiations of air mixtures containing low concentrations of isoprene and NO_x.
- (j) Pulsed laser photolysis of H₂O₂ at 248 nm, in the presence of isoprene/N₂ or isoprene/air mixtures at total pressures in the range 3.8-165 Torr (5.1-220 mbar). Pseudo-first order decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of isoprene (monitored by vacuum UV optical absorption at 184.95 nm). *k* displayed no significant dependence on bath gas or on pressure over the studied range (N.B. The room temperature, 296-298 K, data points presented below were obtained at 3.8, 7.5, 42.9, 71.0, 103 and 165 Torr in N₂ and at 103 and 165 Torr in air. The reported value, tabulated above, is based on the average of the six N₂ determinations).
- (k) Pulsed laser photolysis of H₂O₂ or *t*-C₄H₉OOH at 248 nm, in the presence of isoprene/N₂ or isoprene/N₂/O₂ mixtures. Experiments carried out in either a high pressure apparatus, at total pressures of 1290-1670 Torr (1720-2230 mbar), or in a low pressure apparatus, at total pressures

of 50-140 Torr (66-187 mbar). Decays of HO radical concentrations (monitored by LIF) were characterized in the presence of excess concentrations of isoprene. k displayed no significant dependence pressure or HO radical source, and the tabulated temperature dependence expression is based on the combined dataset, also reported as $k = (10.4 \pm 0.4) \times 10^{-11} (T/298)^{-1.34 \pm 0.12}$. Evidence for H atom abstraction observed from [HO] decays at $T > 700$ K, when the reversible HO addition routes are equilibrated. Based on support from theoretical calculations, and from PTR-TOF-MS measurements of product formation at $m/z = 83$ (attributed to 2-methylene-but-3-enal following abstraction from CH_3 group in the presence of O_2) at 298-473 K, the following expressions were also recommended for high-pressure limiting HO addition (k_{add}) and H abstraction (k_{abs}): $k_{\text{add}} = (9.5 \pm 0.2) \times 10^{-11} (T/298)^{-1.33 \pm 0.07}$; $k_{\text{abs}} = (1.3 \pm 0.3) \times 10^{-11} \exp(-3.61 \text{kJmol}^{-1}/RT)$; where $k = k_{\text{add}} + k_{\text{abs}}$.

- (l) k determined from high pressure measurements. HO generated by H_2O_2 photolysis.
- (m) k determined from low pressure measurements. HO generated by H_2O_2 photolysis.
- (n) k determined from low pressure measurements. HO generated by $t\text{-C}_4\text{H}_9\text{OOH}$ photolysis.
- (o) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of HONO at wavelengths >300 nm. The concentrations of isoprene and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{ethene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 7.78 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K and atmospheric pressure of air (IUPAC, current recommendation).
- (p) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO at wavelengths >300 nm. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{propene}) = 3.81 \pm 0.17$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{propene}) = 2.85 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 299 K and atmospheric pressure of air (IUPAC, current recommendation).
- (q) Relative rate method carried out at atmospheric pressure of $\text{N}_2 + \text{O}_2$. HO radicals were generated by photolysis of H_2O_2 at 253.7 nm. The concentrations of isoprene and 1,3-butadiene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{isoprene})/k(\text{HO} + 1,3\text{-butadiene}) = 1.48 \pm 0.04$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 1,3\text{-butadiene}) = 6.69 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K and atmospheric pressure of air (Atkinson and Arey, 2003).
- (r) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO at wavelengths >300 nm. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{propene}) = 3.81 \pm 0.15$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{propene}) = 2.89 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K and atmospheric pressure of air (IUPAC, current recommendation).
- (s) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO at wavelengths >300 nm. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{propene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{propene}) = 2.87 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K and atmospheric pressure of air (IUPAC, current recommendation).
- (t) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO . The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{trans-butene}) = 1.74 \pm 0.14$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{trans-2-butene}) = 6.40 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and

atmospheric pressure of air (IUPAC, current recommendation). The cited error limits are the 95% confidence intervals (McQuaid et al., 2002).

- (u) Relative rate method carried out in a 192 cm³ volume quartz reaction vessel at atmospheric pressure of helium diluent. HO radicals were generated by photolysis of H₂O₂. The concentrations of isoprene and 2-methylpropene (the reference compound) were measured by MS. Rate coefficients were measured over the temperature ranges 298-363 K by Gill and Hites (2002) and 323-413 K by Hites and Turner (2009). The measured rate coefficient ratios of $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{2-methylpropene})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{2-methylpropene}) = 9.4 \times 10^{-12} \exp(505/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation). The cited Arrhenius expression for the Hites and Turner (2009) study is an un-weighted least-squares fit to their data; the cited error in the temperature dependence is two standard deviations. Combination of the rate coefficients of Gill and Hites (2002) and Hites and Turner (2009) results in the Arrhenius expression $k = 3.12 \times 10^{-11} \exp[(339 \pm 19)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ or, because the combined data suggested a curved Arrhenius plot, $k = 3.44 \times 10^{-17} T^2 \exp[(1037 \pm 14)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Hites and Turner, 2009), both relative to $k(\text{HO} + \text{2-methylpropene}) = 9.4 \times 10^{-12} \exp(505/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- (v) Carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH₃ONO. The concentrations of isoprene and cyclohexane, di-*n*-butyl ether or propene (the reference compounds) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{cyclohexane}) = 14.3 \pm 1.2$ and 1.49 ± 1.3 , $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{di-}n\text{-butyl ether}) = 3.71 \pm 0.14$ and 3.61 ± 0.23 , and $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{propene}) = 3.89 \pm 0.20$, 3.96 ± 0.18 , 3.90 ± 0.15 and 3.98 ± 0.20 are placed on an absolute basis by use of rate coefficients at 298 K and atmospheric pressure of air of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003), $k(\text{HO} + \text{di-}n\text{-butyl ether}) = 2.78 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Mellouki et al., 1995) and $k(\text{HO} + \text{propene}) = 2.86 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation). The value in the table is the un-weighted average together with the two standard deviation error.
- (w) Discharge flow system with MS detection of isoprene and the reference compounds dimethyl disulfide and ethanethiol. HO radicals generated by the reaction F + H₂O. Total pressure was in the range 1-3 Torr (1.3-4 mbar). The rate coefficient for the HO + isoprene reaction was independent of pressure over the range 1-3 Torr at 298 K, but was increased with increasing pressure over the range 1-3 Torr at 340 K. Temperature-dependent rate measurements were carried out at 1.0-1.1 Torr pressure, and hence the rate coefficient at 340 K would have been in the fall-off region. The measured rate coefficient ratios (which were tabulated only at 298 K) were placed on an absolute basis using $k(\text{HO} + \text{dimethyl disulfide}) = 5.9 \times 10^{-11} \exp(380/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Wine et al., 1981) and $k(\text{HO} + \text{ethanethiol}) = 1.23 \times 10^{-11} \exp(396/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Wine et al., 1984). The rate coefficient used for $k(\text{HO} + \text{dimethyl disulfide})$ is slightly different from the current IUPAC recommendation of $7.0 \times 10^{-11} \exp(350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2008), but re-evaluation is only possible for the 298 K rate coefficient (see Comment (x) below).
- (x) Relative to dimethyl disulfide. The measured rate coefficient ratio $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{dimethyl disulfide}) = 0.464 \pm 0.010$ at 298 K is placed on an absolute basis using $k(\text{HO} + \text{dimethyl disulfide}) = 2.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- (y) Relative to ethanethiol. The measured rate coefficient ratio $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{ethanethiol}) = 2.398 \pm 0.043$ at 298 K is placed on an absolute basis using $k(\text{HO} + \text{ethanethiol}) = 4.64 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Wine et al., 1984).

Preferred Values

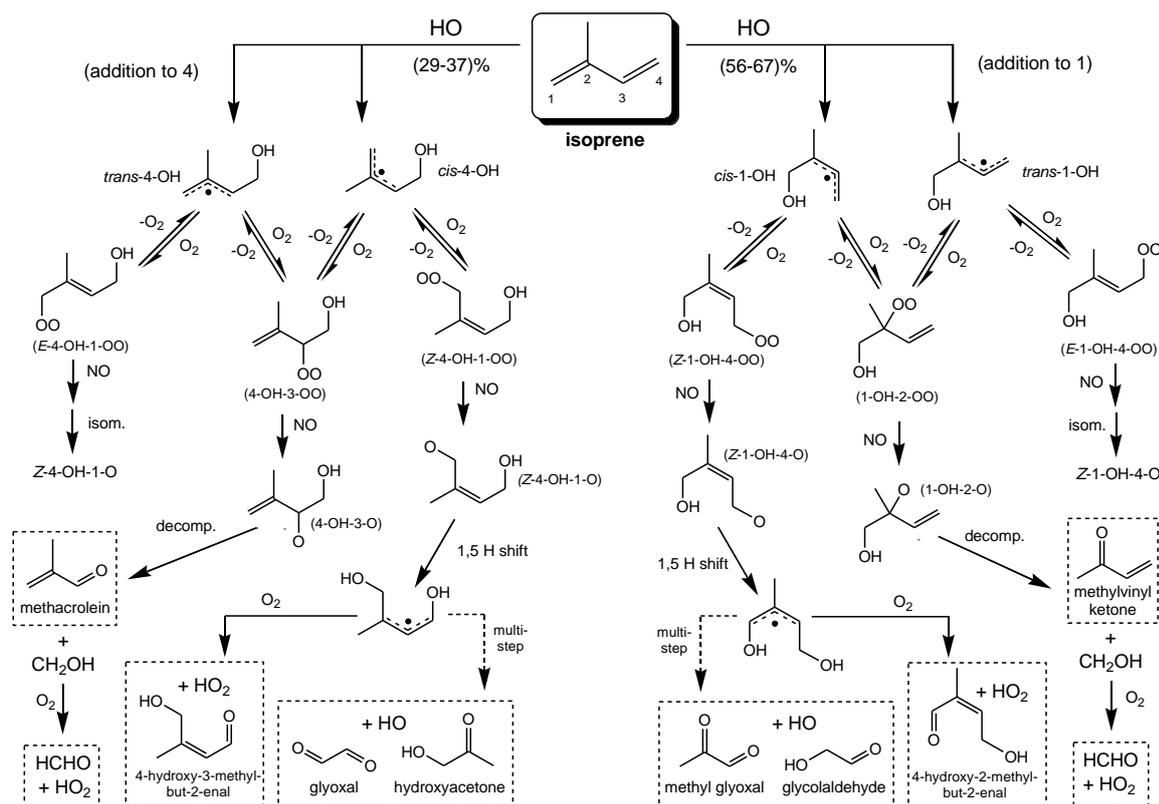
Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.0×10^{-10}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.10 \times 10^{-11} \exp(465/T)$	240-630
<i>Reliability</i>		
$\Delta \log k$	± 0.06	298
$\Delta E/R$	± 150	

Comments on Preferred Values

The reaction of HO radicals with isoprene has been studied extensively, and the room temperature values of k in the reported absolute and relative rate studies are generally in very good agreement. The preferred value of E/R is the average of those reported in the direct studies of Kleindienst et al. (1982), Dillon et al. (2017) and Medeiros et al. (2018), which collectively cover the complete temperature range of the recommendation. The slightly lower values of E/R reported in the direct studies of Siese et al. (1994) and Campuzano-Jost et al. (2000; 2004), and those in the relative rate studies of Gill and Hites (2002) and Singh and Li (2007) also lie within the assigned uncertainty bounds. The 298 K preferred value of k is an average of the room temperature values reported in the direct studies of Kleindienst et al. (1982), Siese et al. (1994), Stevens et al. (1999), Chuong and Stevens (2000; 2002), McGivern et al. (2000), Zhang et al. (2000; 2001), Karl et al. (2004)/Poppe et al. (2007), Dillon et al. (2017) and Medeiros et al. (2018), corrected to 298 K where necessary using the preferred temperature dependence. For each of the related pairs of studies, Chuong and Stevens (2000; 2002), Zhang et al. (2000; 2001) and Karl et al. (2004)/Poppe et al. (2007), a single unweighted average was applied in the above procedure. The rate coefficients reported by Campuzano-Jost et al. (2000; 2004) and Cox et al. (1980) are about 15 % and 27 % lower than the preferred value.

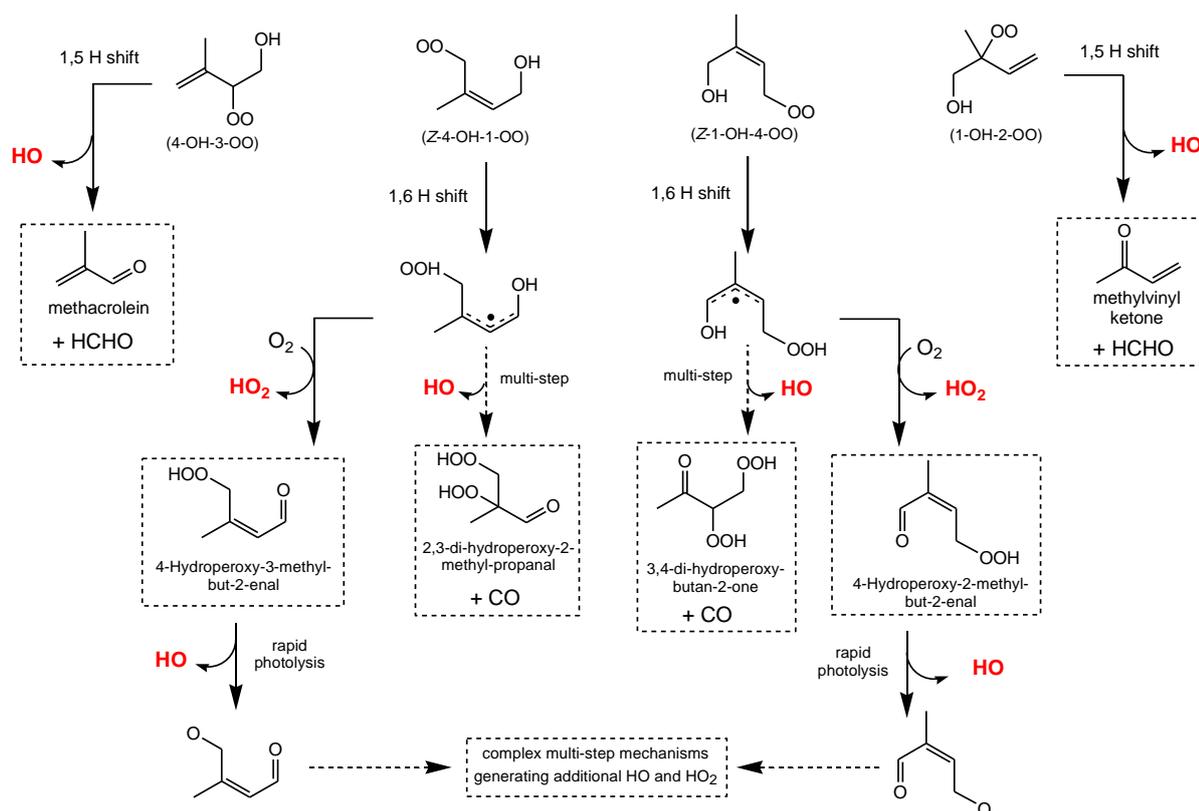
On the basis of theoretical studies (e.g. Vereecken and Peeters, 2001) and structure-activity relationship (SAR) methods (e.g. Jenkin et al., 2018), H atom abstraction has generally been estimated to account for only a very minor fraction (~0.3 %) of the reaction of HO with isoprene at 298 K and 1 bar pressure, with this occurring from the $-\text{CH}_3$ group. This is expected to increase at higher temperatures, and strong evidence for H atom abstraction at $T > 700$ K has been reported by Medeiros et al. (2018) (see comment (k)). They also tentatively suggested that H atom abstraction may account for as much as (3 ± 2) % of the reaction at 298 K, with support from PTR-TOF-MS measurements of product formation at $m/z = 83$, attributed to 2-methylene-but-3-enal. However, this observation may be complicated by formation of the isobaric species, 3-methylfuran, a reported minor product of the HO + isoprene reaction (see below).

The reaction thus proceeds almost exclusively by initial addition of HO to the C=C bonds. Theoretical calculations and SAR methods predict that the percentages of HO radical addition to the 1-, 2-, 3- and 4-position carbon atoms at 298 K lie in the ranges (56–67) %, (2–4) %, (2–5) % and (29–37)%, respectively (e.g. McGivern et al., 2000; Lei et al., 2000; Greenwald et al., 2007; Peeters et al., 2014; Jenkin et al., 2018), with these percentages being relatively insensitive to changes in temperature and pressure over the atmospheric ranges (Greenwald et al., 2007). Addition to the terminal carbon atoms therefore dominates, with subsequent (reversible) addition of O_2 leading to the formation of the six hydroxyallyl peroxy radicals shown in the schematic below (Peeters et al., 2009), with the species nomenclature also based on that study.



The subsequent chemistry has been reviewed in detail by Jenkin et al. (2015) and Wennberg et al. (2018). The majority of reported product studies have traditionally been carried out at atmospheric pressure in the presence of sufficient NO (> 500 ppb), so that the hydroxyallyl peroxy radicals react predominantly with NO at a rate that is much faster than their back decomposition rates. Under these conditions, the chemistry propagated by the reactions with NO forms a number of carbonyl and hydroxycarbonyl end products (shown in boxes), with the following molar yields, e.g. see Jenkin et al. (2015) and Wennberg et al. (2018), and references therein: methyl vinyl ketone, (32–44%), methacrolein (22–28%), formaldehyde (57–66%), 4-hydroxy-2-methyl-but-2-enal and 4-hydroxy-3-methyl-but-2-enal (10–20%), glyoxal (2.1–3%), glycolaldehyde (2.7–4.2%) and hydroxyacetone (2.9–3.8%). Minor formation ($\leq 5\%$) of 3-methylfuran has also been reported (not shown in the schematic). This may be formed from isomerisation and dehydration of the product oxy radicals, Z-1-OH-4-O and Z-4-OH-1-O (Francisco-Márquez et al., 2003), but is also likely formed from secondary cyclisation and dehydration of 4-hydroxy-2-methyl-but-2-enal and 4-hydroxy-3-methyl-but-2-enal, possibly heterogeneously (Dibble, 2007). The reactions of the hydroxyallyl 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 4-15% (see data sheet ROO_50).

Other reactions of the hydroxyallyl 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 (Ruppert and Becker, 2000; Benkelberg et al., 2000; Lee et al., 2005). However, a major advance in understanding in recent years has been the recognition of an important role for unimolecular isomerisation reactions of some of the hydroxyallyl peroxy radical isomers (e.g. Peeters et al., 2009; 2014), namely 1,5 H shift reactions for 1-OH-2-OO and 4-OH-3-OO and, more significantly, 1,6 H shift reactions Z-1-OH-4-OO and Z-4-OH-1-OO, as shown below.



These reactions, in conjunction with interconversion of the hydroxyallyl peroxy radical isomers (*via* the reversible $O_2 + OH$ -isoprene adduct reactions discussed above), provide significant routes for regeneration of HO_x radicals under the low NO_x conditions of the remote atmospheric boundary layer. Usually referred to as the Leuven Isoprene Mechanism (LIM), this subset of the chemistry was originally proposed and characterised in the theoretical studies of Peeters et al. (2009; 2014). It has been largely verified by laboratory experimental studies (Wennberg et al., 2018), and this mechanism and related chemistry continues to be a focus of ongoing experimental and theoretical studies.

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