

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC7

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O₃ + CH₂=C(CH₃)CH=CH₂ (isoprene) → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1.27 × 10 ⁻¹⁷	295 ± 1	Arnts and Gay, 1979	S-CL/GC (a)
7.0 × 10 ⁻¹⁸	260 ± 2	Adeniji et al., 1981	S-CL/GC-FID (a)
1.65 × 10 ⁻¹⁷	294 ± 2		
1.54 × 10 ⁻¹⁴ exp[-(2153 ± 430)/T]	278-323	Atkinson et al., 1982	S-CL/GC-FID (a)
(1.17 ± 0.19) × 10 ⁻¹⁷	296 ± 2		
7.8 × 10 ⁻¹⁵ exp[-(1913 ± 139)/T]	242-323	Treacy et al., 1992	S-CL (a)
(1.28 ± 0.12) × 10 ⁻¹⁷	298		
(8.95 ± 0.25) × 10 ⁻¹⁸	293 ± 2	Grosjean et al., 1993	S-UVA/FTIR (a)
(1.13 ± 0.32) × 10 ⁻¹⁷	291 ± 2	Grosjean and Grosjean, 1996	S-UVA/FTIR (a)
1.30 × 10 ⁻¹⁷	296 ± 2	Neeb et al., 1999	S-FTIR (b)
(1.19 ± 0.09) × 10 ⁻¹⁷	293 ± 2	Klawatsch-Carrasco et al., 2004	S-FTIR (c)
(9.6 ± 0.7) × 10 ⁻¹⁸	286	Karl et al., 2004	S-UVA/GC-FID (d)
(1.24 ± 0.03) × 10 ⁻¹⁷	298 ± 1	Sato et al., 2013	S-FTIR (e)
(1.13 ± 0.17) × 10 ⁻¹⁷	294 ± 2	Ren et al., 2017	S-UVA/FTIR (f)
(9.3 ± 0.7) × 10 ⁻¹⁸	285 ± 2		
(8.6 ± 0.5) × 10 ⁻¹⁸	285 ± 2	Ren et al., 2017	S-UVA/FTIR (a)
<i>Relative Rate Coefficients</i>			
(1.22 ± 0.02) × 10 ⁻¹⁷	296 ± 2	Greene and Atkinson, 1992	RR/GC-FID (g)
9.96 × 10 ⁻¹⁵ exp[-(1973 ± 42)/T]	257-324	Khamaganov and Hites, 2001	RR-MS (h,i)
(1.31 ± 0.08) × 10 ⁻¹⁷	298		
1.69 × 10 ⁻¹⁴ exp[-(2080 ± 120)/T]	242-324	Khamaganov and Hites, 2001	RR-MS (h,j)
(1.56 ± 0.13) × 10 ⁻¹⁷	298		
1.31 × 10 ⁻¹⁴ exp[-(2056 ± 87)/T]	242-324	Khamaganov and Hites, 2001	RR-MS (h,k)
(1.31 ± 0.07) × 10 ⁻¹⁷	298		
9.45 × 10 ⁻¹⁵ exp[-(1963 ± 72)/T]	258-324	Khamaganov and Hites, 2001	RR-MS (h,l)
(1.31 ± 0.08) × 10 ⁻¹⁷	298		
1.43 × 10 ⁻¹⁴ exp[-(2015 ± 149)/T]	278-353	Avzianova and Ariya, 2002	RR/GC-FID (m)
(1.23 ± 0.03) × 10 ⁻¹⁷	298		

Comments

- (a) *k* determined from the observed first-order rate of ozone decay (measured by the first technique shown) in the presence of known excess concentrations of isoprene (measured either by the second technique shown, or with the initial concentration determined by quantified dilution of the pure gas).

- (b) k determined from the observed first-order rate of isoprene decay in the presence of known excess concentrations of ozone, with both reagents measured by FTIR. Cyclohexane added to scavenge HO radicals.
- (c) Both reagents measured by FTIR. Experiments carried out with isoprene in slight excess, in the presence of excess CO as an HO radical scavenger. A value of k was retrieved for each time point during reagent decay in two experiments, based on the observed loss of ozone and the measured concentration of isoprene. The quoted value of k was based on the average of 27 time point determinations.
- (d) k determined from the observed rate of isoprene decay (measured by GC-FID) in the presence of known excess, but changing, concentrations of ozone (measured by UVA), using numerical integration. CO added to scavenge HO radicals.
- (e) k determined from the observed rate of isoprene decay in the presence of known excess, but changing, concentrations of ozone, using numerical integration. Both reagents were measured by FTIR. Experiments were carried out using four HO scavengers (cyclohexane, CO, hexane and diethyl ether), leading to respective values of k (in units $10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) of 1.22 ± 0.07 , 1.24 ± 0.07 , 1.28 ± 0.03 and 1.23 ± 0.09 . The tabulated value is the average of these determinations. A higher value of $(1.47 \pm 0.04) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained in the absence of an HO scavenger.
- (f) k determined from the observed first-order rate of isoprene decay (measured by FTIR) in the presence of known excess concentrations of ozone (measured by UVA). Cyclohexane added to scavenge HO radicals. Rate coefficients approximately 15 % higher value were obtained in the absence of an HO scavenger.
- (g) Relative rate study, with *n*-octane present to scavenge HO radicals. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured value of $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{propene}) = 1.21 \pm 0.02$ is placed on an absolute basis using $k(\text{O}_3 + \text{propene}) = 1.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (h) Relative rate method carried out at 760 Torr (1.013 bar) of helium diluent in a 192 cm^3 volume cylindrical quartz reactor, with ethanol or acetaldehyde being present to scavenge the HO radicals formed. The concentrations of isoprene and the reference compound were monitored by MS.
- (i) With 2-methylpropene as the reference compound. The measured rate coefficient ratios $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + 2\text{-methylpropene})$ are placed on an absolute basis using a rate coefficient of $k(\text{O}_3 + 2\text{-methylpropene}) = 2.92 \times 10^{-15} \exp(-1650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC current recommendation). Note that in Table 3 of Khamaganov and Hites (2001), the rate coefficient ratios stated to be relative to 2-methylpropene appear (Table 7 and Figure 4) to be relative to but-1-ene, and *vice versa*.
- (j) With *cis*-but-2-ene as the reference compound. The measured rate coefficient ratios $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{cis-but-2-ene})$ are placed on an absolute basis using $k(\text{O}_3 + \text{cis-2-butene}) = 3.37 \times 10^{-15} \exp(-970/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC current recommendation).
- (k) With 1-butene as the reference compound. The measured rate coefficient ratios [see Comment (e)] $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{but-1-ene})$ are placed on an absolute basis using $k(\text{O}_3 + 1\text{-butene}) = 3.55 \times 10^{-15} \exp(-1750/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC current recommendation).
- (l) With 2,3-dimethyl-1,3-butadiene as the reference compound. The measured rate coefficient ratios $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + 2,3\text{-dimethyl-but-1,3-diene})$ are placed on an absolute basis using $k(\text{O}_3 + 2,3\text{-dimethyl-1,3-butadiene}) = 6.9 \times 10^{-15} \exp(-1668/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).
- (m) Relative rate study, with 1,3,5-trimethylbenzene present to scavenge HO radicals. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratios were not tabulated, except at room temperature, assumed to be 298 K. The expression $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{propene}) = 2.47 \exp[(135 \pm 149)/T]$, derived from the data, is placed on an absolute basis using $k(\text{O}_3 + \text{propene}) = 5.77 \times 10^{-15} \exp(-1880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation). Note that the 298 K rate coefficient calculated from the reported Arrhenius expression is about 30 % higher than the measured value (see table).

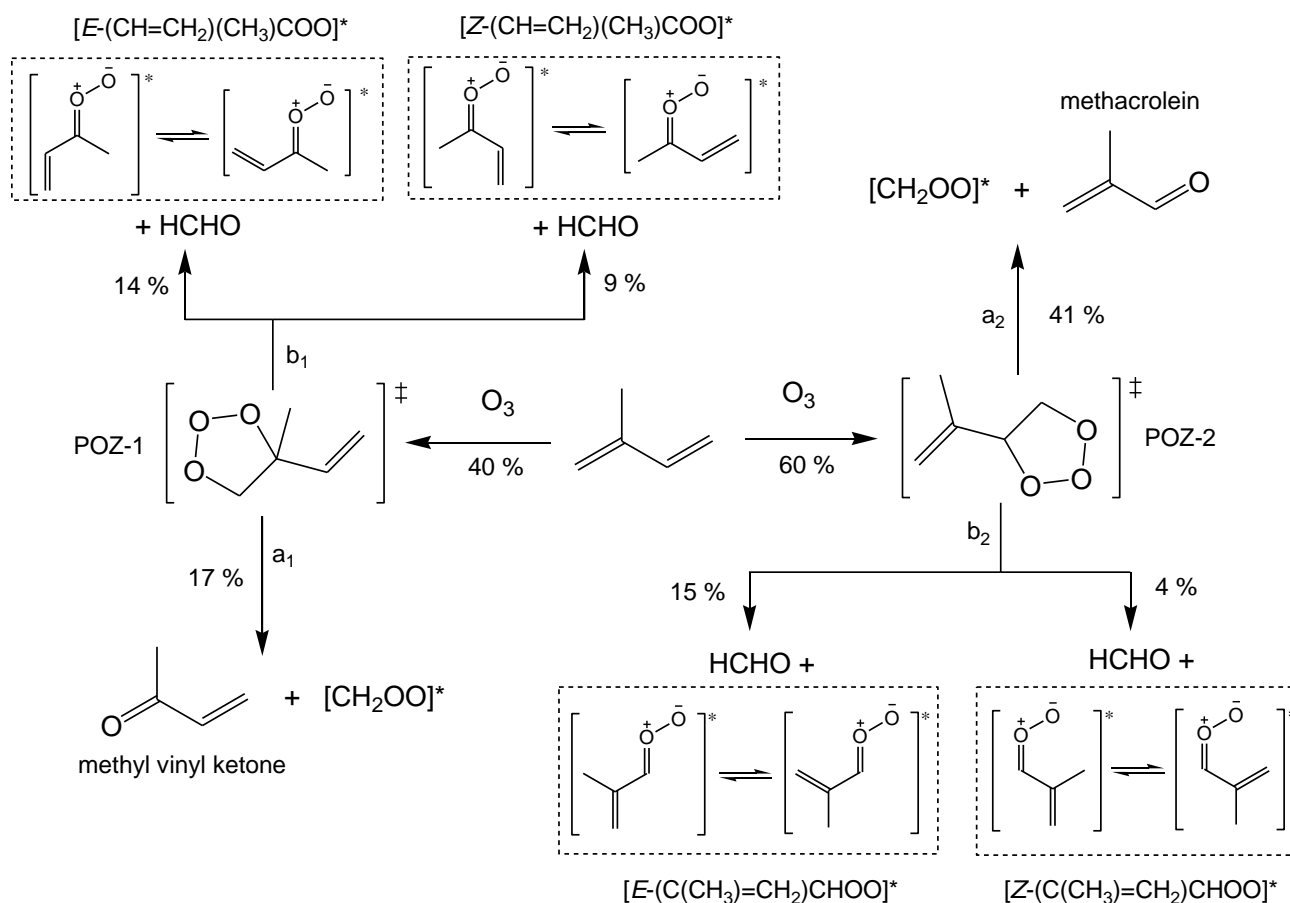
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.28×10^{-17}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.05 \times 10^{-14} \exp(-2000/T)$	240-360
<i>Reliability</i>		
$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 200	240-360

Comments on Preferred Values

The kinetics determinations are in generally good agreement, with consistent values of the temperature coefficient (E/R) reported in a number of studies. The preferred value of E/R is the average of those reported by Treacy et al. (1992), Khamaganov and Hites (2001) and Avzianova and Ariya (2002). The preferred value of k at 298 K is an average of the room temperature determinations reported by Atkinson et al. (1982), Treacy et al. (1992), Greene and Atkinson (1992), Grosjean and Grosjean (1996), Neeb and Moortgat (1999), Khamaganov and Hites (2001), Avzianova and Ariya (2002), Karl et al. (2004), Sato et al. (2013) and Ren et al. (2017), corrected to 298 K, where necessary, using the preferred value of E/R .

It is well established that the reaction proceeds by initial addition of O_3 to either of the $\text{C}=\text{C}$ bonds in the conjugated diene system, forming a pair of energy-rich primary ozonides (POZ-1 and POZ-2) as shown in the schematic below.



POZ-1 rapidly decomposes to form either methyl vinyl ketone and the (excited) Criegee intermediate, $[\text{CH}_2\text{OO}]^*$ (route a_1); or formaldehyde (HCHO) in conjunction with either $[E-(\text{CH}=\text{CH}_2)(\text{CH}_3)\text{COO}]^*$ or $[Z-(\text{CH}=\text{CH}_2)(\text{CH}_3)\text{COO}]^*$ (route b_1). Similarly, POZ-2 decomposes to form either methacrolein and $[\text{CH}_2\text{OO}]^*$ (route a_2); or HCHO in conjunction with either $[E-(\text{C}(\text{CH}_3)=\text{CH}_2)\text{CHOO}]^*$ or $[Z-(\text{C}(\text{CH}_3)=\text{CH}_2)\text{CHOO}]^*$ (route b_2). Reported molar yields of the C_4 carbonyls, methacrolein (0.32 – 0.44) and methyl vinyl ketone (0.13 – 0.18) are consistent with their formation mainly as primary products (e.g. Aschmann and Atkinson, 1994; Grosjean et al., 1993; Rickard et al., 1999; Nguyen et al., 2016). These yields suggest significant contributions from initial addition of O_3 to each $\text{C}=\text{C}$ bond in isoprene, and from decomposition routes a_1 for POZ-1 and a_2 for POZ-2. Reported molar yields of HCHO (0.79 – 0.90; Grosjean et al., 1993; Nguyen et al., 2016) are consistent with the operation of decomposition routes b_1 and b_2 , with HCHO formed directly and from the subsequent chemistry of both sets of C_4 Criegee intermediate and $[\text{CH}_2\text{OO}]^*$. The contributions assigned to the channels in the schematic are taken from Nguyen et al. (2016), and are a combination of their results and information from the literature.

The excited Criegee intermediates may either decompose/isomerize, or be collisionally deactivated to form the corresponding stabilized Criegee intermediates (sCI). A number of relatively recent studies report total sCI yields that are in good agreement, based on scavenging with added SO_2 or H_2O and quantification of the associated products or reagent removal (Sipilä et al., 2014; Newland et al., 2015; Nguyen et al., 2016). We recommend a yield of 0.65 ± 0.10 , based on consideration of these results (see data sheet CGI_21). The information suggests that CH_2OO makes a major contribution to the total, as a result of near-quantitative stabilization of $[\text{CH}_2\text{OO}]^*$. The contribution of the C_4 sCI isomers is therefore believed to be comparatively limited (particularly under atmospheric conditions), partly because they are not stabilized to the same extent as CH_2OO , but also because very rapid unimolecular reactions are estimated to be available for stabilized $Z-(\text{CH}=\text{CH}_2)(\text{CH}_3)\text{COO}$ and $Z-(\text{C}(\text{CH}_3)=\text{CH}_2)\text{CHOO}$ (Vereecken et al., 2017), with decomposition likely also the major fate for $E-(\text{CH}=\text{CH}_2)(\text{CH}_3)\text{COO}$. Based on reported kinetic data (summarised and evaluated in datasheets CGI_1 to CGI_12), the major fate of CH_2OO under tropospheric conditions is expected to be removal via bimolecular reactions, e.g. with $(\text{H}_2\text{O})_2$, NO_2 and SO_2 .

Direct and indirect evidence for the formation of HO radicals has been reported in numerous studies (e.g. Aschmann et al., 1996; Paulson et al., 1998; Neeb and Moortgat, 1999; Malkin et al., 2010; Nguyen et al., 2016; Ren et al., 2017), with yields in the range 0.24-0.28 (preferred value, 0.26 ± 0.04). An important contribution to HO formation is expected to result from (excited or stabilized) $E-(\text{CH}=\text{CH}_2)(\text{CH}_3)\text{COO}$, by an accepted decomposition mechanism involving migration of a β -hydrogen from the $-\text{CH}_3$ group via a vinyl hydroperoxide intermediate (Fenske et al., 2000; Kroll et al., 2001; Barber et al., 2018), also forming the $\text{CH}_2=\text{CHC}(=\text{O})\text{CH}_2$ radical as a co-product. However, additional indirect HO formation may result from the further chemistry of $\text{CH}_2=\text{CHC}(=\text{O})\text{CH}_2$, and following decomposition of the other C_4 Criegee intermediates, as described in the detailed mechanisms presented by Nguyen et al. (2016). These mechanisms also include significant secondary sources of HCHO, and can account for the reported formation of a number of C_1 - C_3 products (e.g. pyruvic acid and methyl glyoxal) in low yields (Grosjean et al., 1993).

References

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- Grosjean et al. (1993)
- ◆ Neeb and Moortgat (1999)
- Karl et al. (2004)
- Ren et al. (2017) isoprene excess
- Greene and Atkinson (1992)
- △ Khamanagov and Hites (2001) relative to cis-but-2-ene
- + Khamanagov and Hites (2001) relative to 2,3-dimethyl-buta-1,3-diene
- - - Avzianova and Ariya (2002) Arrhenius expression
- Adeniji et al. (1981)
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- ▲ Grosjean and Grosjean (1996)
- Klawatsch-Carrasco et al. (2004)
- ◆ Sato et al. (2013)
- Ren et al. (2017) ozone excess
- Khamanagov and Hites (2001) relative to 2-methylpropene
- ◇ Khamanagov and Hites (2001) relative to but-1-ene
- Avzianova and Ariya (2002)
- Recommendation

