

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

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This datasheet last evaluated: December 2007 (with no revision of the preferred values).

O₃ + CH₂=C(CH₃)CH=CH₂ → 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 x 10 ⁻¹⁷	295 ± 1	Arnts and Gay, 1979	S-CL/GC (a)
7.0 x 10 ⁻¹⁸	260 ± 2	Adeniji et al., 1981	S-CL
1.65 x 10 ⁻¹⁷	294 ± 2		
1.1 x 10 ⁻¹⁷	291	Kamens et al., 1982	(b)
1.54 x 10 ⁻¹⁴ exp[-(2153 ± 430)/ <i>T</i>]	278-323	Atkinson et al., 1982	S-CL
(1.17 ± 0.19) x 10 ⁻¹⁷	296 ± 2		
7.8 x 10 ⁻¹⁵ exp[-(1913 ± 139)/ <i>T</i>]	242-323	Treacy et al., 1992	S-UVA
(1.28 ± 0.12) x 10 ⁻¹⁷	298		
(8.95 ± 0.25) x 10 ⁻¹⁸	293 ± 2	Grosjean et al., 1993	S-UVA
(1.13 ± 0.32) x 10 ⁻¹⁷	291 ± 2	Grosjean and Grosjean, 1996	S-UVA
(1.19 ± 0.09) x 10 ⁻¹⁷	293 ± 2	Klawatsch-Carrasco et al., 2004	S-FTIR
(9.6 ± 0.7) x 10 ⁻¹⁸	286	Karl et al., 2004	S-UV/GCMS
<i>Relative Rate Coefficients</i>			
(1.16 ± 0.02) x 10 ⁻¹⁷	296 ± 2	Greene and Atkinson, 1992	RR (c)
9.21 x 10 ⁻¹⁵ exp[-(1955 ± 42)/ <i>T</i>]	257-324	Khamaganov and Hites, 2001	RR (d,e)
(1.29 ± 0.08) x 10 ⁻¹⁷	298		
1.62 x 10 ⁻¹⁴ exp[-(2078 ± 120)/ <i>T</i>]	242-324	Khamaganov and Hites, 2001	RR (d,f)
(1.50 ± 0.13) x 10 ⁻¹⁷	298		
1.24 x 10 ⁻¹⁴ exp[-(2050 ± 87)/ <i>T</i>]	242-324	Khamaganov and Hites, 2001	RR (d,g)
(1.26 ± 0.07) x 10 ⁻¹⁷	298		
9.45 x 10 ⁻¹⁵ exp[-(1963 ± 72)/ <i>T</i>]	258-324	Khamaganov and Hites, 2001	RR (d,h)
(1.35 ± 0.08) x 10 ⁻¹⁷	298		
1.36 x 10 ⁻¹⁴ exp[-(2015 ± 149)/ <i>T</i>]	278-353	Avzianova and Ariya, 2002	RR (i)
(1.22 ± 0.03) x 10 ⁻¹⁷	298		

Comments

- (a) Carried out in one atmosphere of air in 330 liter volume reaction chambers. The O₃ and isoprene concentrations were measured by chemiluminescence and GC, respectively.
- (b) Carried out at atmospheric pressure of air in a large outdoor chamber at night. O₃ was introduced continually over a period of 1.4 hr to an isoprene-air mixture. The isoprene and O₃ concentrations

were monitored by GC and chemiluminescence, respectively, and the rate coefficient obtained by fitting the measured isoprene and O₃ concentrations to a computer model.

- (c) Relative rate study, with *n*-octane being present to scavenge the OH radicals formed from the O₃ reactions. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{propene}) = 1.21 \pm 0.02$ is placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3 + \text{propene}) = 9.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (d) Relative rate method carried out at 760 Torr (1.013 bar) of helium diluent in a 192 cm³ volume cylindrical quartz reactor, with ethanol or acetaldehyde being present to scavenge the OH radicals formed. The concentrations of isoprene and the reference compound were monitored by MS.
- (e) With 2-methylpropene as the reference compound. The measured rate coefficient ratios $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{2-methylpropene})$ are placed on an absolute basis using a rate coefficient of $k(\text{O}_3 + \text{2-methylpropene}) = 2.70 \times 10^{-15} \exp(-1632/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997). 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 1-butene, and *vice versa*.
- (f) With *cis*-2-butene as the reference compound. The measured rate coefficient ratios $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{cis-2-butene})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3 + \text{cis-2-butene}) = 3.22 \times 10^{-15} \exp(-968/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997).
- (g) With 1-butene as the reference compound. The measured rate coefficient ratios [see Comment (e)] $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{1-butene})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3 + \text{1-butene}) = 3.36 \times 10^{-15} \exp(-1744/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997).
- (h) With 2,3-dimethyl-1,3-butadiene as the reference compound. The measured rate coefficient ratios $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{2,3-dimethyl-1,3-butadiene})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3 + \text{2,3-dimethyl-1,3-butadiene}) = 6.9 \times 10^{-15} \exp(-1668/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997).
- (i) Relative rate method carried out at 760 Torr (1.013 bar) of air diluent in a 3 liter volume Pyrex reactor, with 1,3,5-trimethylbenzene being present to scavenge the OH radicals formed. The concentrations of isoprene and propene (the reference compound) were monitored by GC. The measured rate coefficient ratios $k(\text{O}_3 + \text{isoprene})/k(\text{O}_3 + \text{propene})$, which were not tabulated, are placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3 + \text{propene}) = 5.5 \times 10^{-15} \exp(-1880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation). Note that the 298 K rate coefficient calculated from the Arrhenius expression is $1.57 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, 29% higher than the measured value (see table).

Preferred Values

$k = 1.27 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.03 \times 10^{-14} \exp(-1995/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240-360 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta(E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The measured room temperature rate coefficients are in good agreement, as are measured temperature dependencies (Atkinson et al., 1982; Treacy et al., 1992; Khamaganov and Hites, 2001; Avzianova and Ariya, 2002). The preferred temperature dependence is the average of those determined by Treacy et al. (1992), Khamaganov and Hites (2001) and Avzianova and Ariya (2002). The preferred 298 K rate coefficient is the average of the rate coefficients of Atkinson et al. (1982), Treacy et al. (1992), Greene and Atkinson (1992), Grosjean et al. (1993), Grosjean and Grosjean

(1996), Khamaganov and Hites (2001), Avzianova and Ariya (2002), Klawatsch-Carrasco et al. (2004) and Karl et al. (2004), adjusted to 298 K where necessary (Atkinson et al., 1982; Greene and Atkinson, 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1996; Klawatsch-Carrasco et al., 2004; Karl et al., 2004) using the preferred temperature dependence. The preferred temperature dependence is combined with the preferred rate coefficient at 298 K to obtain the pre-exponential factor.

The reaction proceeds by initial addition of O₃ to the C=C bonds to form one of two primary ozonides, which rapidly decompose to form four possible sets of carbonyl + Criegee intermediate (see data sheets on the reactions of O₃ with ethene and propene; IUPAC, 2007). Methacrolein, methyl vinyl ketone and formaldehyde are significant products of this reaction, with measured formation yields of 39-44%, 16-17%, and 90%, respectively (Atkinson and Arey, 2003). HO radicals are also formed from the reaction of O₃ with isoprene, in 25% yield (IUPAC, current recommendation).

References

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- Recommendation
- - - Treacy et al. (1992) Arrhenius fit
- - - Avzianova and Ariya (2002) Arrhenius fit
- Arnts and Gay (1979)
- ▼ Adeniji et al. (1981)
- Kamens et al. (1982)
- ◆ Atkinson et al. (1982)
- ▲ Treacy et al. (1992), at 298 K
- ◆ Greene and Atkinson (1992)
- Grosjean et al. (1993)
- ▼ Grosjean and Grosjean (1996)
- Khamaganov and Hites (2001) vs 2-methylpropene
- ◆ Khamaganov and Hites (2001), vs *cis*-2-butene
- ▲ Khamaganov and Hites (2001), vs 1-butene
- ◆ Khamaganov and Hites (2001), vs 2,3-dimethyl-1,3-butadiene
- Avzianova and Ariya (2002), at 298 K
- ▼ Klawatsch-Carrasco et al. (2004)
- Karl et al. (2004)

