

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox\_VOC3

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This data sheet updated: 19<sup>th</sup> December 2005.



(R=H or CH<sub>3</sub>)

## Product Yield Data

Alkene	Criegee Intermediate(s)	HO Yield (1 bar) ( $\Delta[\text{HO}]/\Delta[\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4]$ )	Reference	Technique/ Comments
Ethene	CH <sub>2</sub> OO	0.18±0.06	Paulson et al., 1999a	Tracer (a)
Ethene	CH <sub>2</sub> OO	0.14±0.07	Rickard et al., 1999	Tracer (b)
Ethene	CH <sub>2</sub> OO	0.20±0.02	Mihelcic et al, 1999	MI-ESR (c)
Ethene	CH <sub>2</sub> OO	(ca. 0.14)	Kroll et al., 2001	Low pressure LIF - see comments (d)
Propene	CH <sub>2</sub> OO, CH <sub>3</sub> CHOO	0.35±0.07	Paulson et al., 1999a	Tracer (a)
Propene	CH <sub>2</sub> OO, CH <sub>3</sub> CHOO	0.32±0.08	Rickard et al., 1999	Tracer (b)
Propene	CH <sub>2</sub> OO, CH <sub>3</sub> CHOO	0.34 <sup>+0.03</sup> <sub>-0.06</sub>	Neeb and Moortgat, 1999	Kinetic/Scavenger (e)
Z-2-butene	CH <sub>3</sub> CHOO	0.33±0.07	McGill et al., 1999	Tracer (b)
Z-2-butene	CH <sub>3</sub> CHOO	0.33±0.05	Orzechowska and Paulson, 2002	Tracer (a)
E-2-butene	CH <sub>3</sub> CHOO	0.61±0.28	Fenske et al., 2000	Tracer (a)
E-2-butene	CH <sub>3</sub> CHOO	0.64±0.12	Orzechowska and Paulson, 2002	Tracer (a)
E-2-butene	CH <sub>3</sub> CHOO	0.54±0.11	McGill et al., 1999	Tracer (b)
E-2-butene	CH <sub>3</sub> CHOO	(ca. 0.60)	Kroll et al., 2001a	Low pressure LIF - see comments (d)
E-2-butene	CH <sub>3</sub> CHOO	0.75±0.19	Siese et al., 2001	LIF (f)
2-Methylpropene	CH <sub>2</sub> OO, (CH <sub>3</sub> ) <sub>2</sub> COO	0.72±0.12	Paulson et al., 1999b	Tracer (a)
2-Methylpropene	CH <sub>2</sub> OO, (CH <sub>3</sub> ) <sub>2</sub> COO	0.60±0.15	Rickard et al., 1999	Tracer (b)
2-Methylpropene	CH <sub>2</sub> OO, (CH <sub>3</sub> ) <sub>2</sub> COO	0.60 <sup>+0.05</sup> <sub>-0.02</sub>	Neeb and Moortgat, 1999	Kinetic/Scavenger (e)
Z-2-Pentene	CH <sub>3</sub> CHOO, CH <sub>3</sub> CH <sub>2</sub> CHOO	0.29±0.06	Orzechowska and Paulson, 2002	Tracer (a)
Z-2-Pentene	CH <sub>3</sub> CHOO, CH <sub>3</sub> CH <sub>2</sub> CHOO	0.27±0.07	Orzechowska and Paulson, 2002	Scavenger (g)
E-2-Pentene	CH <sub>3</sub> CHOO, CH <sub>3</sub> CH <sub>2</sub> CHOO	0.46±0.08	Orzechowska and Paulson, 2002	Tracer (a)
2-Methyl-2-butene	CH <sub>3</sub> CHOO, (CH <sub>3</sub> ) <sub>2</sub> COO	0.93±0.14	Chew and Atkinson, 1996	Scavenger (g)
2-Methyl-2-butene	CH <sub>3</sub> CHOO, (CH <sub>3</sub> ) <sub>2</sub> COO	0.81±0.16	McGill et al., 1999	Tracer (b)
2-Methyl-2-	CH <sub>3</sub> CHOO,	(ca. 0.6)	Kroll et al., 2001a	Low pressure LIF

butene	(CH <sub>3</sub> ) <sub>2</sub> COO				- see comments (d)
2-Methyl-2-butene	CH <sub>3</sub> CHOO, (CH <sub>3</sub> ) <sub>2</sub> COO	0.89±0.22	Siese et al., 2001		LIF (f)
2-Methyl-2-butene	CH <sub>3</sub> CHOO, (CH <sub>3</sub> ) <sub>2</sub> COO	0.98±0.24	Orzechowska and Paulson, 2002		Tracer (a)
2-Methyl-2-butene	CH <sub>3</sub> CHOO, (CH <sub>3</sub> ) <sub>2</sub> COO	0.80±0.12	Orzechowska and Paulson, 2002		Scavenger (a)
2,3-Dimethyl-2-butene	(CH <sub>3</sub> ) <sub>2</sub> COO	0.80±0.12	Chew and Atkinson, 1996		Scavenger (g)
2,3-Dimethyl-2-butene	(CH <sub>3</sub> ) <sub>2</sub> COO	0.89±0.22	Rickard et al., 1999		Tracer (b)
2,3-Dimethyl-2-butene	(CH <sub>3</sub> ) <sub>2</sub> COO	(ca. 1.00)	Kroll et al., 2001a		Low pressure LIF - see comments (d)
2,3-Dimethyl-2-butene	(CH <sub>3</sub> ) <sub>2</sub> COO	1.00±0.25	Siese et al., 2001		LIF (f)
2,3-Dimethyl-2-butene	(CH <sub>3</sub> ) <sub>2</sub> COO	0.91±0.14	Orzechowska and Paulson, 2002		Scavenger (a)
Isoprene (2-methyl-1,3-butadiene )	H <sub>2</sub> COO, H <sub>2</sub> C=C(CH <sub>3</sub> )CHOO	0.25±0.06	Paulson et al., 1998		Tracer (a)
Isoprene (2-methyl-1,3-butadiene )	OOC(CH <sub>3</sub> )CH=CH H <sub>2</sub> COO, H <sub>2</sub> COO, H <sub>2</sub> C=C(CH <sub>3</sub> )CHOO, OOC(CH <sub>3</sub> )CH=CH H <sub>2</sub> COO,	0.26 <sup>+0.03</sup> <sub>-0.06</sub>	Neeb and Moortgat, 1999		Kinetic/Scavenger (e)
Isoprene (2-methyl-1,3-butadiene )	H <sub>2</sub> COO, H <sub>2</sub> C=C(CH <sub>3</sub> )CH OO,OOC(CH <sub>3</sub> )C H=CH <sub>2</sub> H <sub>2</sub> COO,	(ca. 0.25)	Kroll et al., 2001a		Low pressure LIF - see comments (d)
Methylvinyl ketone	H <sub>2</sub> COO, CH <sub>3</sub> C(O)CHOO	0.16±0.08	Aschmann et al., 1996		Scavenger (g)
Methylvinyl ketone	H <sub>2</sub> COO, CH <sub>3</sub> C(O)CHOO	0.16±0.05	Paulson et al., 1998		Tracer (a)
Methacrolein	H <sub>2</sub> COO, HC(O)C(CH <sub>3</sub> )O O	0.20 <sup>+0.10</sup> <sub>-0.13</sub>	Aschmann et al., 1996		Scavenger (g)
α-Pinene	R <sub>1</sub> CHOO, R <sub>2</sub> R <sub>3</sub> COO	0.76±0.11	Chew and Atkinson, 1996		Scavenger (g)
α-Pinene	R <sub>1</sub> CHOO, R <sub>2</sub> R <sub>3</sub> COO	0.70±0.17	Paulson et al., 1998		Tracer (a)
α-Pinene	R <sub>1</sub> CHOO, R <sub>2</sub> R <sub>3</sub> COO	1.00	Pfeiffer et al., 1998		Absorption detection of HO (h)
α-Pinene	R <sub>1</sub> CHOO, R <sub>2</sub> R <sub>3</sub> COO	0.83±0.21	Rickard et al., 1999		Tracer (b)
α-Pinene	R <sub>1</sub> CHOO, R <sub>2</sub> R <sub>3</sub> COO	0.91±0.23	Siese et al., 2001		LIF (f)
β-Pinene	H <sub>2</sub> COO, R <sub>1</sub> R <sub>2</sub> COO	0.24±0.06	Rickard et al., 1999		Tracer (b)
Sabinene	H <sub>2</sub> COO, R <sub>1</sub> R <sub>2</sub> COO	0.33±0.06	Chew and Atkinson, 1996		Scavenger (g)

### Comments

- (a) Small quantities of a tracer compound (1,3,5-trimethylbenzene, *m*-xylene and di-*n*-butyl ether), that react rapidly with HO and very slowly with ozone, were added to the ozone/alkene reaction mixture. HO yields were determined from the diminution in concentration of the added tracer.
- (b) Similar study to comment (b) using 1,3,5-trimethylbenzene as an HO tracer compound.

- (c) Matrix Isolation Electron Spin Resonance (MI-ESR) study in which HO<sub>2</sub> was quantitatively detected. HO was converted to HO<sub>2</sub> by reaction with CO.
- (d) Steady-state HO concentrations in a flow-tube were measured directly by laser induced fluorescence (LIF). The reported HO yields correspond to prompt HO production over short timescales (within *ca.* 30 ms) at total pressures of a few Torr. Although prompt HO yields were seen to decrease rapidly with increasing pressure, the HO yield for 2,3-dimethyl-2-butene at atmospheric pressure was seen to approach the prompt, low-pressure yield over much longer timescales. Thus although the reported yields are for prompt HO production, it is assumed that the long-timescale yields of HO due to thermal decomposition of the carbonyl oxide are the same.
- (e) The rate of alkene consumption was observed under pseudo-first order conditions with an excess concentration of ozone. The decrease in observed rate in the presence of excess cyclohexane (to scavenge any HO formed) was used to derive HO formation yields.
- (f) HO detected by LIF in the EUPHORE outdoor simulation chamber in Valencia. Time-dependent HO and O<sub>3</sub> concentration data were numerically simulated to obtain HO yields.
- (g) Ozonolysis reactions carried out in the presence of sufficient 2-butanol to scavenge  $\geq 95\%$  of all adventitiously formed HO. HO yields derived from the amount of butanone formed. This method superseded earlier experiments in the laboratory of Atkinson and co-workers in which ozonolysis reactions were carried out in the presence of excess cyclohexane, and from which HO formation efficiencies were derived from measured yields of cyclohexanol and cyclohexanone (Atkinson and Aschmann, 1993; Atkinson *et al.*, 1992). However, due to the complex peroxy radical chemistry giving rise to these observed products an uncertainty of around a factor of 1.5 was estimated for the HO yields determined from these studies.

### Preferred Values

Alkene	$k_{(\text{ozone} + \text{alkene})}$ (298 K) / cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Preferred HO yield	References
Ethene	$1.6 \times 10^{-18}$	0.16	Paulson <i>et al.</i> , 1999a; Rickard <i>et al.</i> , 1999
Propene	$1.0 \times 10^{-17}$	0.34	Paulson <i>et al.</i> , 1999a; Rickard <i>et al.</i> , 1999; Neeb and Moortgat, 1999
Z-2-butene	$1.3 \times 10^{-16}$	0.33	McGill <i>et al.</i> , 1999; Orzechowska and Paulson, 2002
E-2-butene	$1.9 \times 10^{-16}$	0.64	McGill <i>et al.</i> , 1999; Orzechowska and Paulson, 2002; Fenske <i>et al.</i> , 2000; Siese <i>et al.</i> , 2001
2-Methylpropene	$1.1 \times 10^{-17}$	0.62	Rickard <i>et al.</i> , 1999; Neeb and Moortgat, 1999; Paulson <i>et al.</i> , 1999b
2-Methyl-2-butene	$4.1 \times 10^{-16}$	0.88	McGill <i>et al.</i> , 1999; Orzechowska and Paulson, 2002; Siese <i>et al.</i> , 2001; Chew and Atkinson, 1996
2,3-Dimethyl-2-butene	$1.1 \times 10^{-15}$	0.90	Rickard <i>et al.</i> , 1999; Orzechowska and Paulson, 2002; Siese <i>et al.</i> , 2001; Chew and Atkinson, 1996
Isoprene	$1.27 \times 10^{-17}$	0.25	McGill <i>et al.</i> , 1999; Paulson <i>et al.</i> , 1998

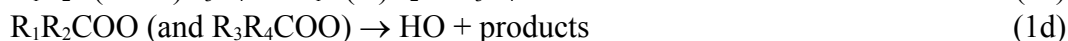
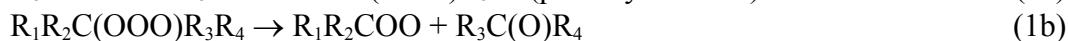
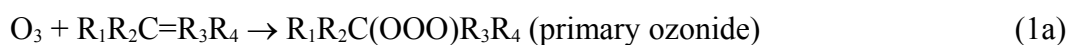
Alkene	$k_{(\text{ozone} + \text{alkene})}$ (298 K) / $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Preferred HO yield	References
$\alpha$ -Pinene	$9.0 \times 10^{-17}$	0.80	Rickard et al., 1999; Siese et al., 2001; Chew and Atkinson, 1996; Paulson et al., 1998

$\Delta \log(\text{yield}) = 0.15$

<sup>a</sup>Rate coefficients taken from the present recommendations or from Atkinson (1997).

### Comments on Preferred Values

The currently accepted mechanism of HO production from ozone-alkene reactions involves the following steps:



Until recently it was generally accepted that HO radicals were produced as a decomposition product of vibrationally excited carbonyl oxide (Criegee) intermediates (Aschmann et al., 1996). In the case of methyl-substituted Criegee intermediates (methylcarbonyl oxide and dimethylcarbonyl oxide) the HO yield varies with the number of methyl-groups in a manner that is consistent with isomerisation of the Criegee intermediate to a hydroperoxide intermediate followed by decomposition and HO release (Rickard et al., 1999; Niki et al., 1987; Martinez and Herron, 1988; Kroll et al., 2001b). However, experimental studies by Kroll et al. (2001a) looked directly at the formation of HO by LIF over short-timescales, as a function of pressure. As the pressure was increased from a few Torr to around atmospheric pressure, the yields of prompt HO (i.e. that formed within 30 ms or so) were seen to decrease to essentially zero. It was concluded that the majority of HO production reported in previous experimental studies of ozone-alkene reactions was due to the thermal decomposition of stabilised Criegee intermediates. This assertion was supported by further LIF studies in which HO production in the ozonolysis of 2,3-dimethyl-2-butene, at one atmosphere of pressure, was seen to increase over significantly longer timescales (Kroll et al., 2001b). A study by Johnson et al. (2001) looked at the HO production efficiency of the reaction of ozone with 2-methyl-2-butene in the presence of relatively high concentrations of scavenger species believed to react with Criegee intermediates. Under the conditions of these latter experiments (with concentrations of scavenger species in excess of those that would be encountered in the troposphere), no effect upon the yield of HO was observed. Thus, it is concluded that, the bimolecular reactions of stabilised Criegee intermediates produced in the ozonolysis of 2-methyl-2-butene (methylcarbonyl oxide and dimethylcarbonyl oxide) will not – under atmospheric conditions – compete with the formation of HO due to their thermal decomposition. It is further concluded that the HO yield measurements summarised above are applicable to the chemistry of the troposphere. The preferred HO yield data listed above are the average values of the measurements for each individual compound.

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