

## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O<sub>x</sub>\_VOC5

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### O<sub>3</sub> + C<sub>2</sub>H<sub>4</sub> → products

#### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$3.3 \times 10^{-15} \exp[-(2365 \pm 101)/T]$	178-233	DeMore, 1969	S-UVA (a)
$1.18 \times 10^{-18}$	298*		
$(1.55 \pm 0.15) \times 10^{-18}$	299	Stedman et al., 1973	S-CL/GC-FID (a)
$9.00 \times 10^{-15} \exp[-(2557 \pm 167)/T]$	235-362	Herron and Huie, 1974	MS/MS (a)
$1.69 \times 10^{-18}$	298*		
$(1.9 \pm 0.1) \times 10^{-18}$	299	Japar et al., 1974, 1976	S-CL/GC-FID (a)
$(1.69 \pm 0.13) \times 10^{-18}$	303	Toby et al., 1976	S-UVA (a)
$4.4 \times 10^{-19}$	260	Adeniji et al., 1981	S-CL/GC-FID (a)
$1.6 \times 10^{-18}$	294		
$(1.43 \pm 0.19) \times 10^{-18}$	296	Atkinson et al., 1982	S-CL/GC-FID (a)
$7.72 \times 10^{-15} \exp[-(2557 \pm 30)/T]$	232-298	Bahta et al., 1984	S-UVA (a)
$(1.45 \pm 0.10) \times 10^{-18}$	298		
$5.1 \times 10^{-15} \exp[-(2446 \pm 91)/T]$	240-324	Treacy et al., 1992	S-CL (a)
$(1.37 \pm 0.08) \times 10^{-18}$	298		
$1.44 \times 10^{-18}$	298	Qi et al., 2006	S-FTIR (a)
$(1.46 \pm 0.13) \times 10^{-18}$	296	Søndergaard et al., 2007	S-FTIR (b)
$(1.35 \pm 0.11) \times 10^{-18}$	298	Wang et al., 2007	S-UVA (a)
$(1.72 \pm 0.35) \times 10^{-18}$	298	Wegener et al., 2007	S-UVA/GC-FID (c),(d)
$(1.45 \pm 0.25) \times 10^{-18}$	298	Alam et al., 2011	S-UVA/FTIR (c),(e)

#### 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 ethene (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 ethene decay in the presence of known excess concentrations of ozone, with both reagents measured by FTIR. Cyclohexane added to scavenge HO radicals.
- (c) Experiments carried out with comparable concentrations of each reagent, in the presence of an HO radical scavenger. The system was simulated using an explicit chemical mechanism, with  $k$  optimized to recreate the observed decays in the concentrations of ozone (measured by the first technique shown) and ethene (measured by the second technique shown).
- (d) CO added to scavenge HO radicals.
- (e) Either CO or cyclohexane added to scavenge HO radicals.

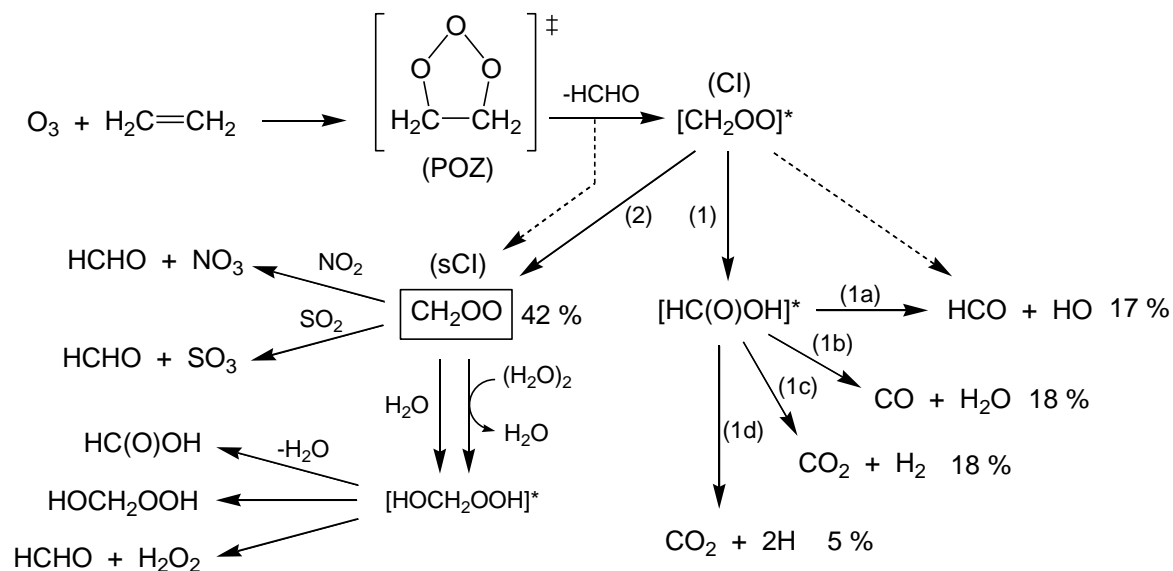
## Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$1.55 \times 10^{-18}$	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$6.82 \times 10^{-15} \exp(-2500/T)$	180-360
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.08$	298
$\Delta E/R$	$\pm 100$	180-360

### Comments on Preferred Values

The absolute kinetics determinations are in generally good agreement, with consistent values of the temperature coefficient ( $E/R$ ) reported in a number of studies covering a wide combined temperature range. The preferred value of  $E/R$  is a rounded average of those reported by DeMore (1969), Herron and Huie (1974), Bahta et al. (1984) and Treacy et al. (1992). The preferred 298 K rate coefficient is an average of the room temperature determinations reported in all the studies tabulated above, corrected to 298 K, where necessary, using the preferred value of  $E/R$ . Note that the 298 K value tabulated here for DeMore et al. (1969) was obtained by extrapolation from the studied temperature range, and was not included in the average.

It is well established that the reaction proceeds by initial addition of  $\text{O}_3$  to form an energy-rich "primary ozonide (POZ)" which rapidly decomposes to form an (excited) Criegee intermediate,  $[\text{CH}_2\text{OO}]^*$  (CI), and formaldehyde, HCHO (e.g. Johnson and Marston, 2008), as represented in the schematic shown below:



The schematic also shows some established features of the further chemistry of  $[\text{CH}_2\text{OO}]^*$ , with suggested contributions of a number of product pathways at 298 K and atmospheric pressure, based on a consensus of the literature. Direct and indirect evidence for the formation of HO radicals has been reported in numerous studies (e.g. Atkinson et al., 1992; Paulson et al., 1999; Rickard et al., 1999; Mihelcic et al., 1999; Fenske et al., 2000; Kroll et al., 2001; Alam et al., 2011), with yields in the range 12–22 % (preferred value,  $17 \pm 5$  %). HO is believed to be formed mainly via an excited dioxirane

intermediate, which isomerises to form “hot” formic acid,  $[\text{HC}(\text{O})\text{OH}]^*$ , before fragmenting to HO and HCO (or HO, H and CO) via reaction (1a) (Kroll et al., 2002; Johnson and Marston, 2008); although a minor contribution from direct decomposition of  $[\text{CH}_2\text{OO}]^*$  (via a four-membered transition state) cannot be ruled out (Calvert et al., 2000). Formation of  $\text{HO}_2$  radicals has also been reported (Mihelcic et al., 1999; Qi et al., 2006; Wegener et al., 2007; Alam et al., 2011), with yields in the range 10–50 % (preferred value,  $\sim 27$  %). It can be formed from the reactions of  $\text{O}_2$  with H and HCO, which are produced in reactions (1a) and (1d). The associated chemistry in reactions (1a)-(1d) also produces CO and  $\text{CO}_2$ , and the relative contributions assigned to these product pathways are consistent with reported CO and  $\text{CO}_2$  yields (e.g. Su et al., 1981; Atkinson, 1990; Thomas et al., 1993; Neeb et al., 1998).

There have been numerous determinations of the yield of the stabilized Criegee intermediate,  $\text{CH}_2\text{OO}$  (sCI), mainly based on addition of scavengers ( $\text{H}_2\text{O}$ , CO, HCHO, HCOOH,  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$  and  $\text{SO}_2$ ) to the system and quantification of the associated reaction products (Su et al., 1980; Kan et al., 1981; Hatakeyama et al., 1984; 1986; Horie and Moortgat, 1991; Neeb et al., 1996; 1998; Horie et al., 1999; Hasson et al., 2001; Alam et al., 2011; Newland et al., 2015).  $\text{CH}_2\text{OO}$  yields in the range 35–54 % have been obtained at room temperature and atmospheric pressure (preferred value,  $42 \pm 10$  %). The yield appears to display a dependence on total pressure, with a significant fraction of stabilised  $\text{CH}_2\text{OO}$  reported to be formed at low pressures (Hatakeyama et al., 1986). By extrapolation of measurements made down to 13 mbar, they found the yield to be reduced by about a factor of two at zero pressure, suggesting significant ( $\sim 20$  %) direct formation of stabilised  $\text{CH}_2\text{OO}$  (and HCHO) from the decomposition of POZ.

Based on reported kinetic data (summarised and evaluated in datasheets CGI\_1 to CGI\_12), the major fate of  $\text{CH}_2\text{OO}$  under tropospheric conditions is expected to be removal via bimolecular reactions, e.g. with  $(\text{H}_2\text{O})_2$ ,  $\text{NO}_2$  and  $\text{SO}_2$ , as illustrated in the schematic above.

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- Recommendation

