

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC6

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O₃ + C₃H₆ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
1.26×10^{-17}	295	Cox and Penkett, 1972	S-CL/GC-FID (a)
$(1.25 \pm 0.10) \times 10^{-17}$	299	Stedman et al., 1973	S-CL/GC-FID (a)
$6.14 \times 10^{-15} \exp[-(1897 \pm 109)/T]$	235-362	Herron and Huie, 1974	MS/MS (a),(b)
1.06×10^{-17}	298*		
$(1.3 \pm 0.1) \times 10^{-17}$	299	Japar et al., 1974, 1976	S-CL/GC-FID (a)
5.1×10^{-18}	260	Adeniji et al., 1981	S-CL/GC-FID (a)
1.26×10^{-17}	294		
$(1.04 \pm 0.14) \times 10^{-17}$	296	Atkinson et al., 1982	S-CL/GC-FID (a)
$4.9 \times 10^{-15} \exp[-(1858 \pm 70)/T]$	240-324	Treacy et al., 1992	S-CL (a)
$(9.4 \pm 0.4) \times 10^{-18}$	298		
1.15×10^{-17}	296 ± 2	Neeb and Moortgat, 1999	S-FTIR (c)
$5.8 \times 10^{-15} \exp[-(1907 \pm 53)/T]$	282-314	Jia et al., 2006	S-UVA/GC-FID (a)
1.01×10^{-17}	300		
$(1.06 \pm 0.12) \times 10^{-17}$	298	Wegener et al., 2007	S-UVA/GC-FID (d)

Comments

- 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 propene (measured either by the second technique shown, or with the initial concentration determined by quantified dilution of the pure gas).
- Due to a typographical error, the lowest temperature studied was 235.0 K and not 250.0 K as stated in Table 2 of Herron and Huie (1974).
- k determined from the observed first-order rate of propene decay in the presence of known excess concentrations of ozone, with both reagents measured by FTIR. Cyclohexane added to scavenge HO radicals.
- Experiments carried out with comparable concentrations of each reagent, in the presence of excess CO as 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 propene (measured by the second technique shown).

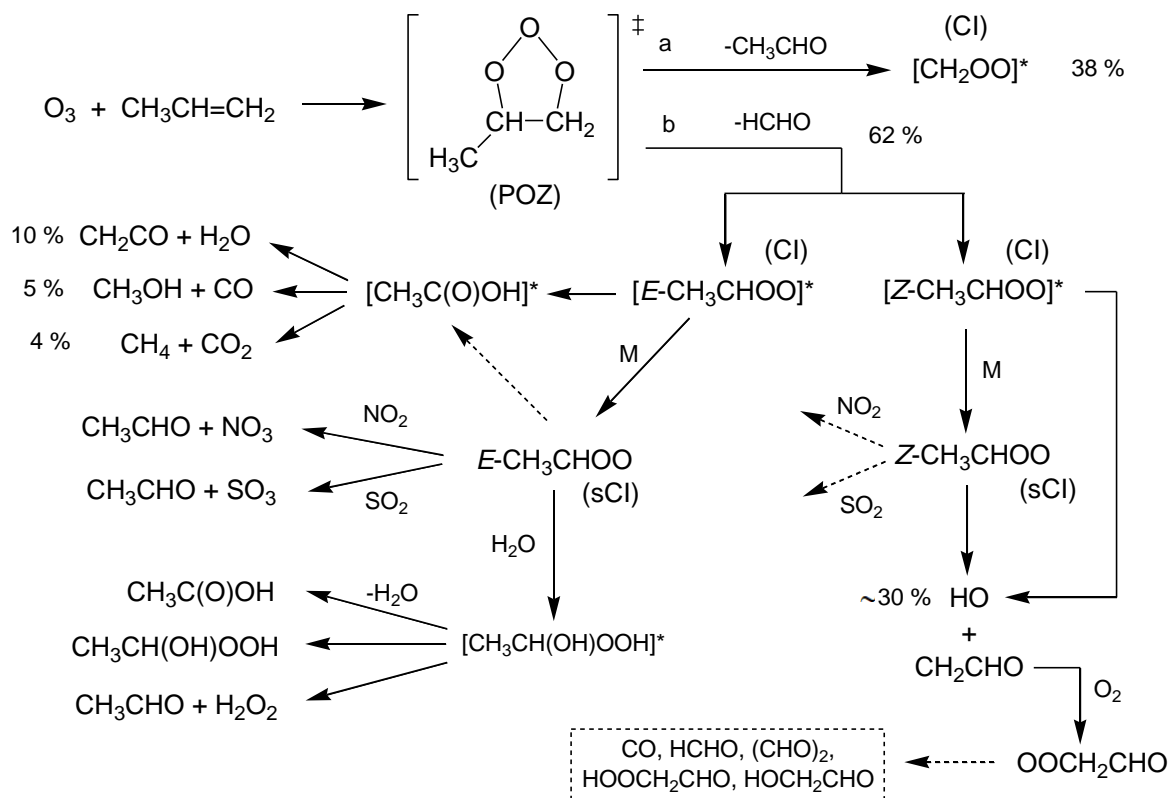
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.05×10^{-17}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$5.77 \times 10^{-15} \exp(-1880/T)$	230-370
<i>Reliability</i>		
$\Delta \log k$	± 0.15	298
$\Delta E/R$	± 100	230-370

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. The preferred value of E/R is a rounded average of those reported by Herron and Huie (1974) and Treacy et al. (1992), which is also consistent with those reported by Adeniji et al. (1981) and Jia et al. (2006) over narrow temperature ranges. The preferred value of k at 298 K is an average of the room temperature determinations reported by Herron and Huie (1974), Atkinson et al. (1982), Treacy et al. (1992), Neeb and Moortgat (1999), Jia et al. (2006) and Wegener et al. (2007), corrected to 298 K, where necessary, using the preferred value of E/R . The other tabulated determinations are consistent with this recommendation, being about 20-30 % higher than the preferred value.

It is well established that the reaction proceeds by initial addition of O_3 to form an energy-rich "primary ozonide (POZ)" which rapidly decomposes to form two sets of "primary" carbonyl product plus (excited) Criegee intermediate, as shown in the schematic below. Reported primary yields of acetaldehyde (CH_3CHO) and formaldehyde (HCHO) suggest important contributions from both decomposition channels, (a) and (b), with $k_b/(k_a+k_b)$ lying in the range 0.60-0.65 (Horie and Moortgat 1991; Grosjean et al., 1996; Tuazon et al., 1997; Rickard et al., 1999), consistent with the values given in the schematic.



The further chemistry of $[\text{CH}_2\text{OO}]^*$, formed from channel (a), is expected to follow the pathways described in the data sheet for the $\text{O}_3 + \text{C}_2\text{H}_4$ reaction (Ox_VOC5), although their relative importance is not necessarily the same. Channel (b) forms either $[\text{E-CH}_3\text{CHOO}]^*$ or $[\text{Z-CH}_3\text{CHOO}]^*$, in conjunction with HCHO. The schematic above shows some established features of the further chemistry of these excited Criegee intermediates, with suggested contributions of a number of product pathways at 298 K and atmospheric pressure, based on a consensus of the literature. They may either decompose via a number of possible pathways, or be collisionally deactivated to form the corresponding stabilized Criegee intermediates (sCI), i.e. $\text{E-CH}_3\text{CHOO}$ and $\text{Z-CH}_3\text{CHOO}$ (Fenske et al., 2000a).

Direct and indirect evidence for the formation of HO radicals has been reported in numerous studies (e.g. Atkinson and Aschmann, 1993; Neeb and Moortgat, 1999; Paulson et al., 1999; Rickard et al., 1999; Aschmann et al., 2003; Wegener et al., 2007; Qi et al., 2009; Alam et al., 2013), with yields in the range 30–40 % (preferred value, 36 ± 4 %). HO is expected to be formed mainly from either $[\text{Z-CH}_3\text{CHOO}]^*$ or $\text{Z-CH}_3\text{CHOO}$, by an accepted decomposition mechanism involving abstraction of a β -hydrogen via a vinyl hydroperoxide intermediate (Fenske et al., 2000b; Kroll et al., 2001), also forming the vinoxy radical (CH_2CHO) as a co-product. A minor contribution to HO formation may also result from decomposition of $[\text{CH}_2\text{OO}]^*$. Assuming that the relative importance of the reaction pathways for $[\text{CH}_2\text{OO}]^*$ formed from propene are similar to those for $[\text{CH}_2\text{OO}]^*$ formed from ethene, this contribution is estimated to be about 6 %, suggesting that decomposition of $[\text{Z-CH}_3\text{CHOO}]^*$ and $\text{Z-CH}_3\text{CHOO}$ contributes about 30 %. The vinoxy radical (CH_2CHO) reacts with O_2 under atmospheric conditions. At 1 bar, this is expected to form a stabilized peroxy radical, which can undergo conventional bimolecular reactions (e.g. with NO, HO_2 and other peroxy radicals) to form a number of products as shown, including secondary HCHO and glyoxal, $(\text{CHO})_2$, which has been reported to be formed with a yield of about 3 % (Tuazon et al., 1997). At pressures below about 270 mbar, the (chemically-activated) peroxy radical adduct has also been reported to decompose (e.g. to form $\text{HO} + \text{HCHO} + \text{CO}$), thereby providing a small secondary source of HO radicals (Oguchi et al., 2004).

Evidence for the decomposition pathways for $[\text{E-CH}_3\text{CHOO}]^*$ shown in the schematic (proceeding via formation of “hot” acetic acid, $[\text{E-CH}_3\text{C}(\text{O})\text{OH}]^*$) has been reported by Tuazon et al. (1997), with the suggested contributions based on the yields of methane (CH_4), methanol (CH_3OH) and ketene (CH_2CO) reported in that study.

The total yield of stabilized Criegee intermediates (sCI) in the system ($\text{CH}_2\text{OO} + \text{E-CH}_3\text{CHOO} + \text{Z-CH}_3\text{CHOO}$) at atmospheric pressure has been reported to be about 25 % by Hatakayama et al. (1984), based on scavenging with added SO_2 and quantification of the product H_2SO_4 (preferred value, 25 ± 10 %). Assuming that the relative importance of the reaction pathways for $[\text{CH}_2\text{OO}]^*$ formed from propene are similar to those for $[\text{CH}_2\text{OO}]^*$ formed from ethene, CH_2OO makes a significant estimated contribution (~ 16 %) to the total sCI yield.

Based on reported kinetic data (summarised and evaluated in datasheets CGI_15 to CGI_17), the major fate of $\text{E-CH}_3\text{CHOO}$ under tropospheric conditions is expected to be removal via bimolecular reactions, in particular with H_2O , as illustrated in the schematic above. The major fate of $\text{Z-CH}_3\text{CHOO}$ is expected to be thermal decomposition, as described above.

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