

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O_x_VOC17

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O₃ + *cis*-but-2-ene → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
1.41×10^{-16}	296	Cox and Penkett, 1972	S-CL/GC-FID (a)
$(1.05 \pm 0.32) \times 10^{-16}$	298	Finlayson et al., 1974	S-UVA/GC-FID (a)
$(1.61 \pm 0.07) \times 10^{-16}$	299 ± 2	Japar et al., 1974	S-CL/GC-FID (a)
$3.11 \times 10^{-15} \exp[-(956 \pm 54)/T]$	225-364	Huie and Herron, 1975	MS/MS (a)
1.26×10^{-16}	298*		
$(1.38 \pm 0.16) \times 10^{-16}$	297 ± 1	Atkinson et al., 1983	S-CL/GC-FID (a)
$3.4 \times 10^{-15} \exp[-(979 \pm 22)/T]$	240-324	Treacy et al., 1992	S-CL (a)
$(1.23 \pm 0.18) \times 10^{-16}$	298		
$(1.29 \pm 0.11) \times 10^{-16}$	298	Wegener et al., 2007	S-UVA/GC-FID (b)
<i>Relative Rate Coefficients</i>			
$(1.29 \pm 0.08) \times 10^{-16}$	296 ± 2	Greene and Atkinson, 1992	RR/GC-FID (c)

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 *cis*-but-2-ene (measured either by the second technique shown, or with the initial concentration determined by quantified dilution of the pure gas).
- 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 *cis*-but-2-ene (measured by the second technique shown).
- Relative rate study, with *n*-octane present to scavenge HO radicals. The concentrations of *cis*-but-2-ene and propene (the reference compound) were measured by GC. The measured value of $k(\text{O}_3 + \textit{cis}\text{-but-2-ene})/k(\text{O}_3 + \textit{propene}) = 12.8 \pm 0.8$ is placed on an absolute basis using $k(\text{O}_3 + \textit{propene}) = 1.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

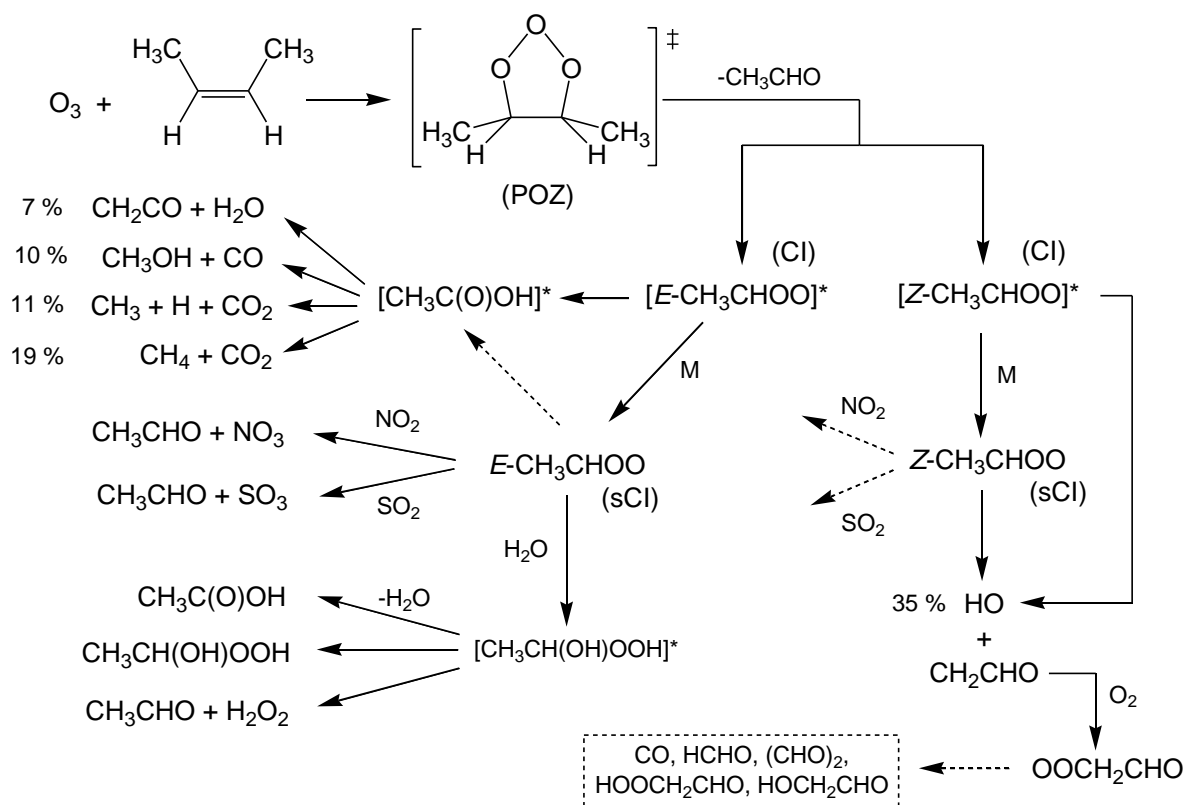
Preferred Values

Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	1.3×10^{-16}	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.37 \times 10^{-15} \exp(-970/T)$	220-370
<i>Reliability</i>		
$\Delta \log k$	± 0.05	298
$\Delta E/R$	± 200	220-370

Comments on Preferred Values

The kinetics determinations are in generally good agreement. The preferred value of E/R is based on the average of those reported by Huie and Herron (1975) and Treacy et al. (1992), which are in good agreement. The preferred value of k at 298 K is an average of the room temperature determinations reported by Huie and Herron (1975), Atkinson et al. (1983), Treacy et al. (1992), Greene and Atkinson (1992) and Wegener et al. (2007), corrected to 298 K, where necessary, using the preferred value of E/R . These values agree to within $\pm 7\%$ of the preferred value. The earlier tabulated determinations of Cox and Penkett (1972), Finlayson et al. (1974) and Japar et al. (1974) are also consistent with this recommendation, deviating by less than 25% from 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 acetaldehyde, CH_3CHO , and one or other of the (excited) Criegee intermediate conformers, $[\text{E}-\text{CH}_3\text{CHOO}]^*$ and $[\text{Z}-\text{CH}_3\text{CHOO}]^*$, as represented in the schematic shown below. Some features of the further chemistry are also shown, with suggested approximate contributions of a number of product pathways at 298 K and atmospheric pressure inferred from reported end product studies.



It should be noted that the contributions of the pathways differ from those suggested for [*E*-CH₃CHOO]* and [*Z*-CH₃CHOO]* formed from the reactions of O₃ with both propene (datasheet Ox_VOC6) and *trans*-but-2-ene (datasheet Ox_VOC18), indicating that the fates of the Criegee intermediates are probably sensitive to their level of excitation, and that this can differ from one system to another. [*E*-CH₃CHOO]* and [*Z*-CH₃CHOO]* may either decompose via a number of possible pathways, or be collisionally deactivated to form the corresponding stabilized Criegee intermediates (sCI), i.e. *E*-CH₃CHOO and *Z*-CH₃CHOO (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; McGill et al., 1999; Orzechowska and Paulson, 2002; Wegener et al., 2007; Alam et al., 2013), with yields in the range 18–41 % (preferred value, 33 ± 7 %). HO is expected to be formed mainly from either [*Z*-CH₃CHOO]* or *Z*-CH₃CHOO, 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 (CH₂CHO) as a co-product. CH₂CHO reacts with O₂ 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, HO₂ and other peroxy radicals) to form a number of products as shown. These include HCHO which has been reported to be formed with yields in the range 13-18 % in a number of studies (Horie et al., 1994; 1997; Grosjean et al., 1996; Tuazon et al., 1997) and glyoxal, (CHO)₂, which has been reported to be formed with a yield of about 7 % (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 HO + HCHO + CO), thereby providing a small secondary source of HO radicals (Oguchi et al., 2004).

Evidence for the decomposition pathways for [*E*-CH₃CHOO]* shown in the schematic (proceeding via formation of “hot” acetic acid, [*E*-CH₃C(O)OH]*) has been reported in a number of studies, with the suggested contributions approximately based on the yields of CO₂, methane (CH₄), methanol (CH₃OH) and ketene (CH₂CO) reported by Tuazon et al. (1997) and Horie et al. (1997), and HO₂ (formed from reaction of H with O₂) reported by Alam et al. (2013).

The total yield of stabilized Criegee intermediates (*E*-CH₃CHOO and *Z*-CH₃CHOO) in the system has been reported to be 18 % by Niki et al. (1977), based on scavenging with added HCHO and quantification of the propene ozonide product. Consistent with this, CH₃CHO yields slightly greater than unity (1.1-1.2) have been reported in a number of studies in the presence of H₂O (Grosjean et al., 1996; Tuazon et al., 1997; Wegener et al., 2007), suggesting a CH₃CHO yield of about 10-20 % from the reactions of sCI under these conditions. Based on the reported rate coefficients for their reactions with H₂O, and the relatively rapid decomposition of *Z*-CH₃CHOO, it is possible that only *E*-CH₃CHOO is scavenged significantly by reaction with H₂O in these studies.

Based on reported kinetic data (summarised and evaluated in datasheets CGI_15 to CGI_17), the major fate of *E*-CH₃CHOO under tropospheric conditions is expected to be removal via bimolecular reactions, in particular with H₂O, as illustrated in the schematic above. The major fate of *Z*-CH₃CHOO is expected to be thermal decomposition, as described above.

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