

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet O<sub>x</sub>\_VOC18

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## O<sub>3</sub> + *trans*-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>			
$2.57 \times 10^{-16}$	296	Cox and Penkett, 1972	S-CL/GC-FID (a)
$(2.75 \pm 0.23) \times 10^{-16}$	$299 \pm 2$	Stedman et al., 1973	S-CL (a)
$(2.60 \pm 0.09) \times 10^{-16}$	$299 \pm 2$	Japar et al., 1974	S-CL/GC-FID (a)
$5.96 \times 10^{-15} \exp[-(1051 \pm 43)/T]$	225-364	Huie and Herron, 1975	MS/MS (a)
$1.76 \times 10^{-16}$	298*		
$(2.56 \pm 0.15) \times 10^{-16}$	$299 \pm 2$	Japar et al., 1976	S-CL/GC-FID (a),(b)
$2.88 \times 10^{-16}$	$294 \pm 2$	Adeniji et al., 1981	S-CL (a)
$6.7 \times 10^{-15} \exp[-(1066 \pm 115)/T]$	240-324	Treacy et al., 1992	S-CL (a)
$(1.81 \pm 0.06) \times 10^{-16}$	298		
$(2.38 \pm 0.15) \times 10^{-16}$	298	Wegener et al., 2007	S-UVA/GC-FID (c)
<i>Relative Rate Coefficients</i>			
$(2.10 \pm 0.10) \times 10^{-16}$	$297 \pm 2$	Nolting et al., 1988	RR/GC-FID (d)
$(2.17 \pm 0.15) \times 10^{-16}$	$296 \pm 2$	Greene and Atkinson, 1992	RR/GC-FID (e)
$5.86 \times 10^{-15} \exp[-(1149 \pm 54)/T]$	278-353	Avzianova and Ariya, 2002	RR/GC-FID (f)
$(1.86 \pm 0.12) \times 10^{-16}$	298		

### 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 *trans*-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 in air and helium diluent gas. The rate coefficient in the table is that measured in air. A slightly higher rate coefficient of  $(2.83 \pm 0.07) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was measured in helium diluent, consistent with data from a comprehensive study of the effects of O<sub>2</sub> on the measured rate coefficients for O<sub>3</sub> + propene, which showed that secondary reactions occurred in the absence of O<sub>2</sub>.
- 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 *trans*-but-2-ene (measured by the second technique shown).
- The concentrations of *trans*-but-2-ene and *cis*-but-2-ene (the reference compound) were measured in the presence of O<sub>3</sub> by GC. It appears from the publication that an HO radical scavenger was not present. The measured rate coefficient ratio  $k(\text{O}_3 + \textit{trans}\text{-but-2-ene})/k(\text{O}_3 + \textit{cis}\text{-but-2-ene})$  is placed

on an absolute basis using  $k(\text{O}_3 + \text{cis-but-2-ene}) = 1.29 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 297 K (IUPAC, current recommendation).

- (e) Relative rate study, with *n*-octane present to scavenge HO radicals. The concentrations of *trans*-but-2-ene and propene (the reference compound) were measured by GC. The measured value of  $k(\text{O}_3 + \text{trans-but-2-ene})/k(\text{O}_3 + \text{propene}) = 21.5 \pm 1.5$  is placed on an absolute basis using  $k(\text{O}_3 + \text{propene}) = 1.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K (IUPAC, current recommendation).
- (f) Relative rate method carried out at 760 Torr (1.013 bar) of air diluent in a 3 L volume Pyrex reactor, with 1,3,5-trimethylbenzene being present to scavenge the HO radicals formed. The concentrations of *trans*-but-2-ene and *cis*-but-2-ene (the reference compound) were monitored by GC. The measured rate coefficient ratios were placed on an absolute basis by Avzianova and Ariya (2002) using the Arrhenius expression of Treacy et al. (1992) for  $\text{O}_3 + \text{cis-but-2-ene}$ . The measured rate coefficient ratios were not tabulated, except at room temperature, assumed to be 298 K. The rate coefficient ratio  $k(\text{O}_3 + \text{trans-but-2-ene})/k(\text{O}_3 + \text{cis-but-2-ene}) = 1.74 \exp[-(179 \pm 54)/T]$ , derived from the data provided in Avzianova and Ariya (2002), is placed on an absolute basis using  $k(\text{O}_3 + \text{cis-but-2-ene}) = 3.37 \times 10^{-15} \exp(-970/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (IUPAC, current recommendation). The 298 K rate coefficient calculated from the Arrhenius expression ( $1.24 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) is a factor of 1.5 lower than the room temperature rate coefficient cited by Avzianova and Ariya (2002). The Arrhenius expression reported by Avzianova and Ariya (2002) therefore appears to be in error.

### Preferred Values

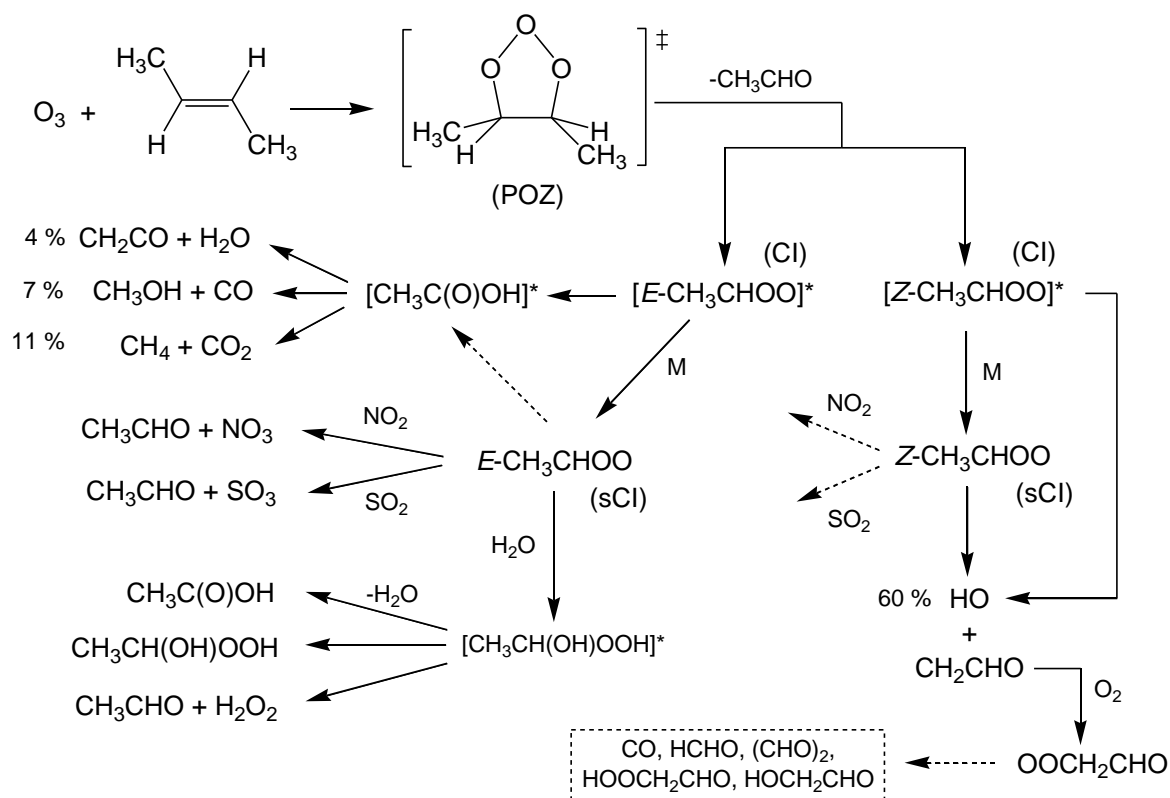
Parameter	Value	T/K
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.0 \times 10^{-16}$	298
$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$7.0 \times 10^{-15} \exp(-1060/T)$	220-370
<i>Reliability</i>		
$\Delta \log k$	$\pm 0.1$	298
$\Delta E/R$	$\pm 200$	220-370

### Comments on Preferred Values

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 Arrhenius parameters given by Avzianova and Ariya (2002) are inconsistent with the reported room temperature value of  $k$  (see comment (f)), although their value of  $E/R$  lies within the uncertainty bounds assigned to the preferred value.

There is some disagreement in the reported room temperature values of  $k$ . The preferred value of  $k$  at 298 K is based on the average of the direct determinations of Huie and Herron (1975), Treacy et al. (1992) and Wegener et al. (2007) and the relative rate determinations of Greene and Atkinson (1992) and Avzianova and Ariya (2002), corrected to 298 K, where necessary, using the preferred value of  $E/R$ . These values are in reasonable agreement, lying within  $\pm 20\%$  of the preferred value. The relative rate experiments of Nolting et al. (1988) were apparently carried out without an ozone scavenger, although their reported value of  $k$  is consistent with the recommendation. The remaining absolute determinations report values of  $k$  lying about 30-50% higher than the preferred value.

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 acetaldehyde,  $\text{CH}_3\text{CHO}$ , and one or other of the (excited) Criegee intermediate conformers,  $[E\text{-CH}_3\text{CHOO}]^*$  and  $[Z\text{-CH}_3\text{CHOO}]^*$ , 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-CH<sub>3</sub>CHOO]\* and [Z-CH<sub>3</sub>CHOO]\* formed from the reactions of O<sub>3</sub> with both propene (datasheet Ox\_VOC6) and *cis*-but-2-ene (datasheet Ox\_VOC17), 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-CH<sub>3</sub>CHOO]\* and [Z-CH<sub>3</sub>CHOO]\* may either decompose via a number of possible pathways, or be collisionally deactivated to form the corresponding stabilized Criegee intermediates (sCI), i.e. E-CH<sub>3</sub>CHOO and Z-CH<sub>3</sub>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; McGill et al., 1999; Orzechowska and Paulson, 2002; Hasson et al., 2003; Wegener et al., 2007; Alam et al., 2013), with yields in the range 54–64 % (preferred value, 60 ± 6 %) reported at atmospheric pressure. Similar yields have also been reported at low pressures by Donahue et al. (1998), (68 ± 9) %, and Kroll et al. (2001), ~ 60 %. HO is expected to be formed mainly from either [Z-CH<sub>3</sub>CHOO]\* or Z-CH<sub>3</sub>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<sub>2</sub>CHO) as a co-product. CH<sub>2</sub>CHO reacts with O<sub>2</sub> 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<sub>2</sub> 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 13–29 % in a number of studies (Horie et al., 1994; 1997; Grosjean et al., 1996; Tuazon et al., 1997) and glyoxal, (CHO)<sub>2</sub>, which has been reported to be formed with a yield of about 10 % (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-CH<sub>3</sub>CHOO]\* shown in the schematic (proceeding via formation of “hot” acetic acid, [E-CH<sub>3</sub>C(O)OH]\*) has been reported in a number of studies, with the suggested contributions approximately based on the yields of methane (CH<sub>4</sub>), methanol (CH<sub>3</sub>OH) and

ketene ( $\text{CH}_2\text{CO}$ ) reported by Tuazon et al. (1997) and Horie et al. (1997). However, the reported yields of  $\text{CO}_2$  in the same studies (about 23–29%) are not fully accounted for by these contributions.

There have been a number of determinations of the yield of the stabilized Criegee intermediates (*E*- $\text{CH}_3\text{CHOO}$  and *Z*- $\text{CH}_3\text{CHOO}$ ), mainly based on addition of scavengers ( $\text{H}_2\text{O}$ ,  $\text{SO}_2$  and  $\text{CF}_3\text{C}(\text{O})\text{CF}_3$ ) to the system and quantification of the associated reaction products (Hatekayama and Akimoto, 1994; Rickard et al., 1999; Horie et al., 1999; Hasson et al., 2001). The reported yields lie in the range 13–24 % (preferred value 18 %). Consistent with this,  $\text{CH}_3\text{CHO}$  yields slightly greater than unity (1.1–1.2) have been reported in a number of studies in the presence of  $\text{H}_2\text{O}$  (Grosjean et al., 1996; Tuazon et al., 1997; Hasson et al., 2001), suggesting a  $\text{CH}_3\text{CHO}$  yield of about 10–20 % from the reactions of sCI under these conditions. Based on the reported rate coefficients for their reactions with  $\text{H}_2\text{O}$ , and the relatively rapid decomposition of *Z*- $\text{CH}_3\text{CHOO}$ , it is possible that only *E*- $\text{CH}_3\text{CHOO}$  is scavenged significantly by reaction with  $\text{H}_2\text{O}$  in these studies.

Based on reported kinetic data (summarised and evaluated in datasheets CGI\_15 to CGI\_17), the major fate of *E*- $\text{CH}_3\text{CHOO}$  under tropospheric conditions is expected to be removal via bimolecular reactions, in particular with  $\text{H}_2\text{O}$ , as illustrated in the schematic above. The major fate of *Z*- $\text{CH}_3\text{CHOO}$  is expected to be thermal decomposition, as described above.

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