IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC16

This datasheet last evaluated: July 2018; last change in preferred values: July 2018

O_3 + but-1-ene $\rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.23 \pm 0.04) \times 10^{-17}$	299 ± 2	Japar et al., 1974	S-CL/GC-FID (a)
2.93×10^{-15} exp[-(1686 $\pm$ 20)/T]	225-363	Huie and Herron, 1975	MS/MS (a)
1.03×10^{-17}	298*		
5.3×10^{-18}	260 ± 2	Adeniji et al., 1981	S-CL/GC-FID (a)
1.24×10^{-17}	294 ± 2		
3.7×10^{-15} exp[-(1801 $\pm$ 155)/T]	240-324	Treacy et al., 1992	S-CL (a)
$(8.8 \pm 0.6) \times 10^{-18}$	298		
$(9.64 \pm 0.87) \times 10^{-18}$	298	Wegener et al., 2007	S-UVA/GC-FID (b)
3.5×10^{-15} exp[-(1756 $\pm$ 84)/T]	294.9-350.2	Shi et al., 2011	S-UVA (a)
9.66×10^{-18}	298*		
Relative Rate Coefficients			
$(9.85 \pm 0.03) \times 10^{-18}$	296 ± 2	Greene and Atkinson, 1992	RR/GC-FID (c)
4.0×10^{-15} exp[-(1754 $\pm$ 46)/T]	278-353	Avzianova and Ariya, 2002	RR/GC-FID (d)
$(1.14 \pm 0.09) \times 10^{-17}$	298		

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 but-1-ene (measured either by the second technique shown, or with the initial concentration determined by quantified dilution of the pure gas).

(b) 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 but-1-ene (measured by the second technique shown).

(c) Relative rate study, with *n*-octane present to scavenge HO radicals. The concentrations of but-1-ene and propene (the reference compound) were measured by GC. The measured value of k(O$_3$ + but-1-ene)/k(O$_3$ + propene) = 0.975 $\pm$ 0.030 is placed on an absolute basis using k(O$_3$ + propene) = 1.01 $\times$ 10^{-17} cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

(d) Relative rate study, with 1,3,5-trimethylbenzene present to scavenge HO radicals. The concentrations of but-1-ene and propene (the reference compound) were measured by GC. The measured rate coefficient ratios were not tabulated. The expression k(O$_3$ + but-1-ene)/k(O$_3$ + propene) = 0.694 exp[(126 $\pm$ 46)/T], derived from the data, is placed on an absolute basis using k(O$_3$ + propene) = 5.77 $\times$ 10^{-15} exp(-1880/T) cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.0×10^{-17}	298
k /cm^3 molecule^{-1} s^{-1}	3.55×10^{-15} exp(-1750/T)	220-370

Reliability

$\Delta \log k$	± 0.08	298
$\Delta E/R$	± 200	220-370

Comments on Preferred Values

The 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 the average of those reported by Huie and Herron (1975), Treacy et al. (1992), Avzianova and Ariya (2002) and Shi et al. (2011), which is also consistent with the relative values reported at 260 K and 294 K by Adeniji et al. (1981). The preferred value of *k* at 298 K is an average of the room temperature determinations reported by Huie and Herron (1975), Treacy et al. (1992), Greene and Atkinson (1992), Avzianova and Ariya (2002), Wegener et al. (2007) and Shi et al. (2011), 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" 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 propanal (C$_2$H$_5$CHO) and formaldehyde (HCHO) suggest important contributions from both decomposition channels, (a) and (b), with $k_b/(k_a+k_b) \approx 0.65$ (Grosjean et al., 1996; Paulson et al., 1999; Hasson et al., 2001).
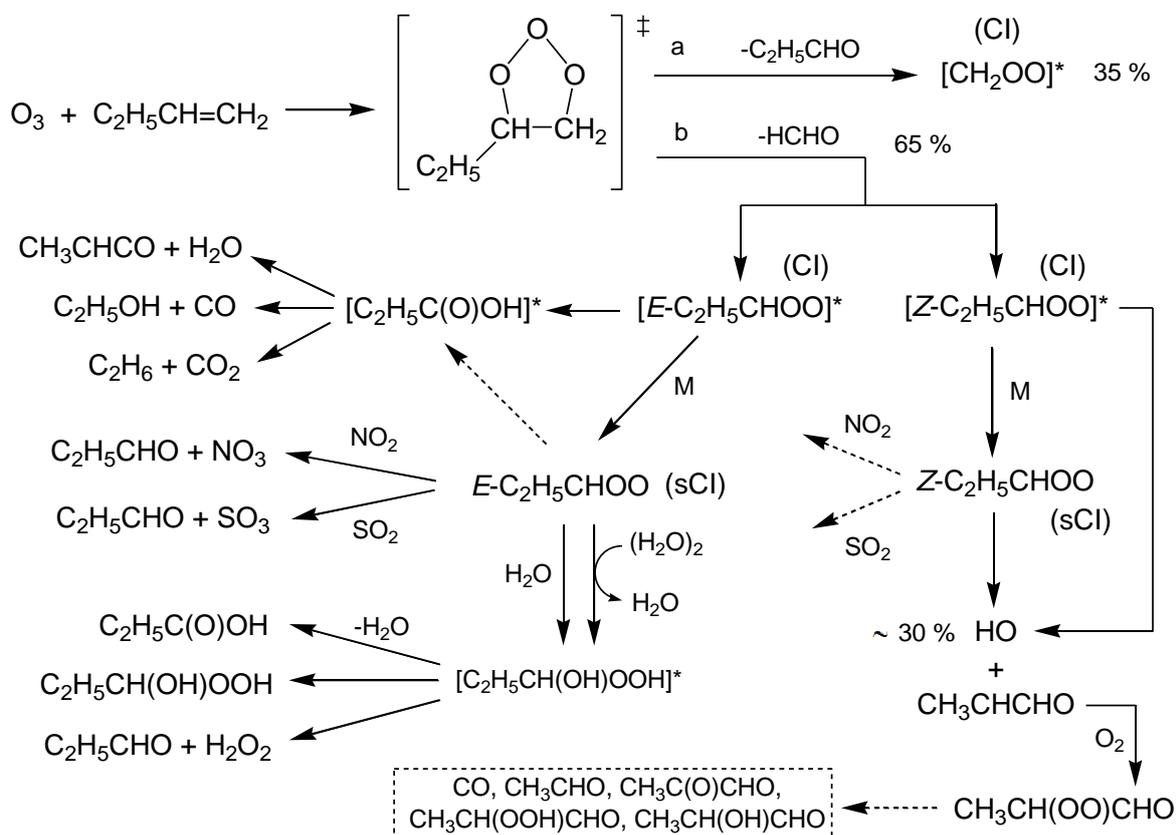
The further chemistry of [CH$_2$OO]* is expected to follow the pathways described in the data sheet for the O$_3$ + C$_2$H$_4$ reaction (Ox_VOC5), although their relative importance is not necessarily the same. Channel (b) forms either [E-C$_2$H$_5$CHOO]* or [Z-C$_2$H$_5$CHOO]*, in conjunction with HCHO. The schematic above shows some probable features of the further chemistry of these excited Criegee intermediates, based partly by analogy with E- and Z- [CH$_3$CHOO]* conformers formed in the O$_3$ + C$_3$H$_6$ system (Ox_VOC6). Where shown, product yields are appropriate to 298 K and atmospheric pressure. [E-C$_2$H$_5$CHOO]* and [Z-C$_2$H$_5$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-C$_2$H$_5$CHOO and Z-C$_2$H$_5$CHOO (Fenske et al., 2000a).

Direct and indirect evidence for the formation of HO radicals has been reported in several studies (e.g. Atkinson and Aschmann, 1993; Paulson et al., 1999; Fenske et al., 2000b; Wegener et al., 2007; Alam et al., 2013), with yields in the range 26–56 % (preferred value, 38 ± 18 %). HO is expected to be formed mainly from either [Z-C$_2$H$_5$CHOO]* or Z-C$_2$H$_5$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 2-methylvinoxy radical (CH$_3$CHCHO) as a co-product. A minor contribution to HO formation may also result from decomposition of [CH$_2$OO]*. Assuming that the relative importance of the reaction pathways for [CH$_2$OO]* formed from but-1-ene are similar to those for [CH$_2$OO]* formed from ethene, this contribution is estimated to be about 6 %, suggesting that decomposition of [Z-C$_2$H$_5$CHOO]* and Z-C$_2$H$_5$CHOO contributes about 30 %. The 2-methylvinoxy radical (CH$_3$CHCHO) reacts with O$_2$ under atmospheric conditions (Oguchi et al., 2001). 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. No direct evidence has been reported for the other decomposition pathways shown for [E-C$_2$H$_5$CHOO]* (proceeding via formation of "hot" propanoic acid, [CH$_3$C(O)OH]*), but they are inferred from the corresponding products reported for the reaction of ozone with propene (see datasheet Ox_VOC6).

The total yield of stabilized Criegee intermediates (sCI) in the system (CH$_2$OO + E-C$_2$H$_5$CHOO + Z-C$_2$H$_5$CHOO) has been reported to be 27 % by Hasson et al. (2001), based on scavenging with added H$_2$O and quantification of the yields of associated products (HOCH$_2$OOH, C$_2$H$_5$CHO and H$_2$O$_2$). Assuming that the relative importance of the reaction pathways for [CH$_2$OO]* formed from but-1-ene are similar to those for [CH$_2$OO]* formed from ethene, CH$_2$OO makes a significant estimated contribution (∼ 15 %) to the total sCI yield.

The major fate of E-CH$_3$CHOO under tropospheric conditions is expected to be removal via bimolecular reactions, particularly with H$_2$O and (H$_2$O)$_2$, as illustrated in the schematic above. The major fate of Z-C$_2$H$_5$CHOO is expected to be thermal decomposition, as described above.

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