Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC32

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O_3 + (β-caryophyllene) → products
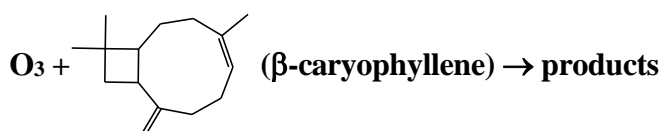
Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.2 \pm 1.0) \times 10^{-14}$	295 ± 2	Richters et al., 2015	S-IR/UVA (a)
Relative Rate Coefficients			
$(8.71 \pm 1.23) \times 10^{-15}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(c)
$(1.09 \pm 0.07) \times 10^{-14}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(d)
$(1.02 \pm 0.03) \times 10^{-14}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (b),(e)
$(2.7 \pm 1.9) \times 10^{-15}$	366 ± 2	Ghalaieny et al., 2012	RR-GC (f)
$(1.39 \pm 0.38) \times 10^{-14}$	295 ± 2	Richters et al., 2015	RR-GC-MS (g)
$(1.19 \pm 0.21) \times 10^{-14}$	295 ± 2	Richters et al., 2015	RR-MS (h)

β-caryophyllene is 4,11,11-trimethyl-8-methylene-bicyclo[7.2.0]undec-4-ene

Comments

(a) *k* determined from the observed rate of ozone decay (measured by UVA at 254 nm) in the presence of known starting concentrations of β-caryophyllene (measured by FT-IR), in stopped-flow experiments at a total pressure of ~1 bar, with sufficient propane to scavenge >99 % of HO radicals. It was not possible to temporally-resolve the ozone decay under pseudo-first order conditions for highly-reactive sesquiterpenes such as β-caryophyllene. The experiments were therefore carried out with comparable starting concentrations of ozone and β-caryophyllene, and the results were solved numerically using an extrapolation method connected with a Newton-technique for parameter estimation.

(b) The concentrations of β-caryophyllene and 2-methyl-but-2-ene, 2,3-dimethyl-but-2-ene or terpinolene (the reference compounds), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in 6400–6900 L all Teflon chambers at 740 Torr (990 mbar) pressure of purified air in the presence of O_3. The measured rate coefficient ratios, $k(O_3 + $ β-caryophyllene$)/k(O_3 + $ 2-methyl-but-2-ene$) = (22.0 \pm 3.1)$, $k(O_3 + $ β-caryophyllene$)/k(O_3 + $ 2,3-dimethyl-but-2-ene$) = (9.98 \pm 0.60)$ and $k($β-caryophyllene$)/k(O_3 + $ terpinolene$) = (6.40 \pm 0.20)$, are placed on an absolute basis using $k(O_3 + $ 2-methyl-but-2-ene$) = 3.96 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003); $k(O_3 + $ 2,3-dimethyl-but-2-ene$) = 1.09 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 296 K and $k(O_3 + $ terpinolene$) = 1.6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendations). The final value of *k* quoted by

the authors was based on the more precise measurements relative to 2,3-dimethyl-but-2-ene and terpinolene.

(c) Relative to 2-methyl-but-2-ene.

(d) Relative to 2,3-dimethyl-but-2-ene.

(e) Relative to terpinolene.

(f) The concentrations of β-caryophyllene and 2,3-dimethyl-but-2-ene (the reference compound), with excess cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 123 L Teflon-coated chamber at 780 Torr (1040 mbar) pressure of N_2, with repeated injections of O_3/O_2. The measured rate coefficient ratio, $k(O_3 + \text{β-caryophyllene})/k(O_3 + \text{2,3-dimethyl-but-2-ene}) = 2.04$, is placed on an absolute basis using $k(O_3 + \text{2,3-dimethyl-but-2-ene}) = 1.32 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 366 K (IUPAC, current recommendation). It is noted that the authors used a much lower value of $k(O_3 + \text{2,3-dimethyl-but-2-ene}) = 2.89 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}, based on a relative rate measurement reported in the same study, leading to a reported value of $k = (5.9 \pm 4.2) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 366 K.

(g) The concentrations of β-caryophyllene and α-terpinene (the reference compound), with 2-methylpropene to scavenge HO radicals, were monitored by GC-MS in a flow tube at atmospheric pressure. The measured rate coefficient ratio, $k(O_3 + \text{β-caryophyllene})/k(O_3 + \text{α-terpinene}) = (0.73 \pm 0.04)$, is placed on an absolute basis using $k(O_3 + \text{α-terpinene}) = 1.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(h) The concentrations of β-caryophyllene and 2,3-dimethyl-but-2-ene (the reference compound), with propane to scavenge HO radicals, were monitored by PTR-MS in a flow tube at atmospheric pressure. The measured rate coefficient ratio, $k(O_3 + \text{β-caryophyllene})/k(O_3 + \text{2,3-dimethyl-but-2-ene}) = (10.9 \pm 0.8)$, is placed on an absolute basis using $k(O_3 + \text{2,3-dimethyl-but-2-ene}) = 1.09 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 295 K (IUPAC, current recommendation).

Preferred Values

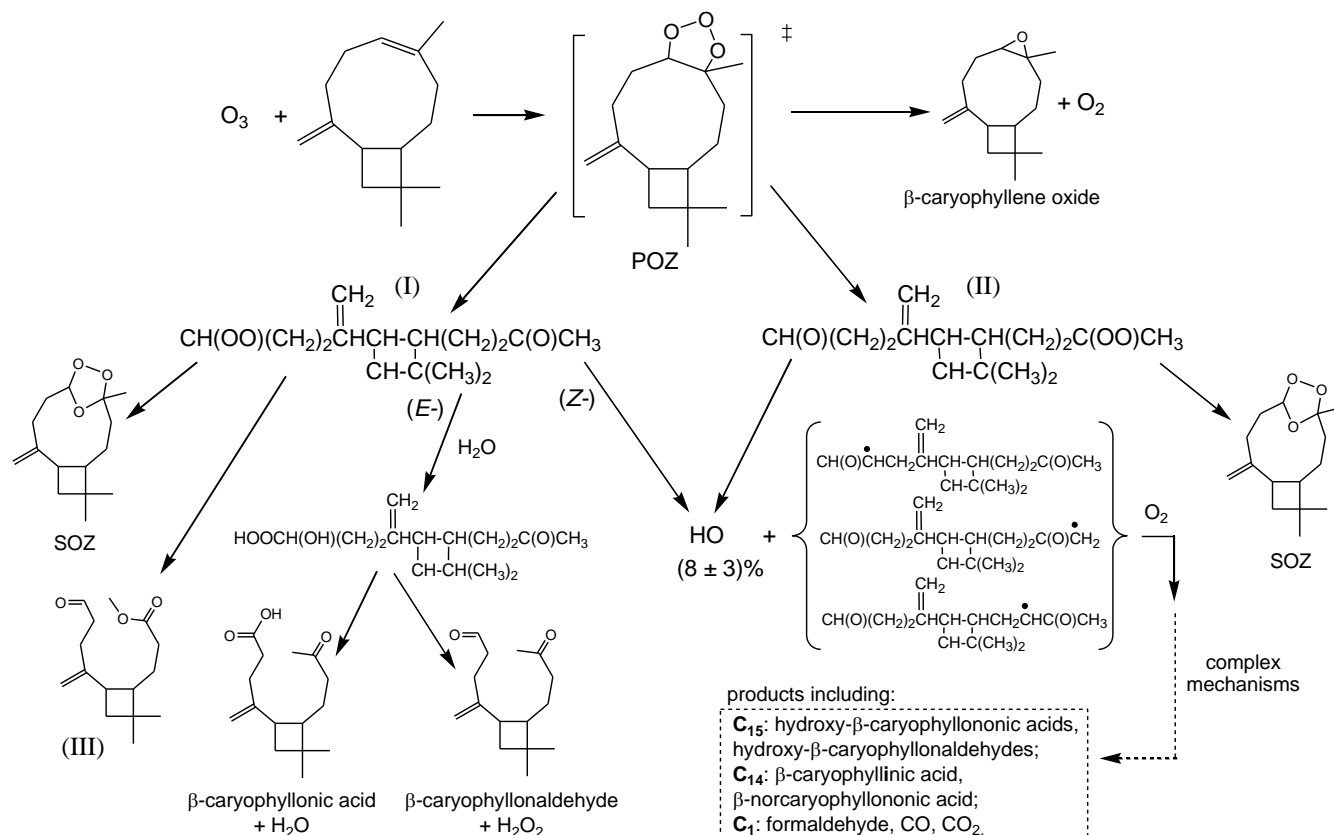| Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.2×10^{-14}	298
Reliability		
$\Delta \log k$	± 0.15	298

Comments on Preferred Values

The preferred value of the rate coefficient at 298 K is based on an average of the more precise determinations of Shu and Atkinson (1994), as favoured by the authors (see comment (b)), and the relative rate coefficient determinations of Richters et al. (2015), which are in good agreement and consistent with the approximate absolute rate coefficient determination of Richters et al. (2015). The preferred value of k is also consistent with that calculated theoretically by Nguyen et al. (2009), who predicted that the reaction has a weak negative temperature dependence near room temperature described by the expression $k = 8.3 \times 10^{-24}$ T$^{3.05}$ exp(1082/T) cm^3 molecule^{-1} s^{-1}, such that $k = 9.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 298 K. The lower approximate value reported by Ghalaieny et al. (2012) at 366 K was interpreted by the authors in terms of heterogeneous interferences of secondary organic aerosol (SOA) formation, leading to overestimates in previously-reported room temperature determinations. However, the more recent consistent results of Richters et al. (2015) using low reagent concentrations in the absence of SOA formation appear to disprove this hypothesis.

The reaction may proceed by initial addition of O_3 to either of the endocyclic or exocyclic C=C bonds in β-caryophyllene. Comparison of k for the reaction of ozone with β-caryophyllene with that reported for

the suite of oxidation products that retain the originally exocyclic C=C bond (Winterhalter et al., 2009), suggests that the reaction of O_3 with β-caryophyllene occurs predominantly ($\approx$ 99 %) at the endocyclic bond. Support for this comes from the distribution of products reported in a number of studies.

The addition of O_3 to the endocyclic C=C bond in β-caryophyllene forms a "primary ozonide (POZ)". Although minor (~1 %) formation of β-caryophyllene oxide has been reported (Calogirou et al., 1997; Jaoui et al., 2003), it is likely that POZ mainly decomposes to form the two carbonyl-substituted Criegee intermediates ((I) and (II)), as represented in the schematic below.

O_3 +

POZ

β-caryophyllene oxide + O_2

(I)
CH_2
$CH(OO)(CH_2)_2CHCH\text{-}CH(CH_2)_2C(O)CH_3$
$CH\text{-}C(CH_3)_2$

(II)
CH_2
$CH(O)(CH_2)_2CHCH\text{-}CH(CH_2)_2C(OO)CH_3$
$CH\text{-}C(CH_3)_2$

SOZ

SOZ

(E-)

(Z-)

H_2O

CH_2
$HOOCH(OH)(CH_2)_2CHCH\text{-}CH(CH_2)_2C(O)CH_3$
$CH\text{-}CH(CH_3)_2$

HO + (8 ± 3)%

O_2

complex mechanisms

(III)

β-caryophyllonic acid + H_2O

β-caryophyllonaldehyde + H_2O_2

CH_2
$CH(O)\overset{\bullet}{C}HCH_2CHCH\text{-}CH(CH_2)_2C(O)CH_3$
$CH\text{-}C(CH_3)_2$

CH_2
$CH(O)(CH_2)_2CHCH\text{-}CH(CH_2)_2C(O)\overset{\bullet}{C}H_2$
$CH\text{-}C(CH_3)_2$

CH_2
$CH(O)(CH_2)_2CHCH\text{-}CHCH_2\overset{\bullet}{C}HC(O)CH_3$
$CH\text{-}C(CH_3)_2$

products including:
C_{15}: hydroxy-β-caryophyllononic acids, hydroxy-β-caryophyllonaldehydes;
C_{14}: β-caryophyllinic acid, β-norcaryophyllononic acid;
C_1: formaldehyde, CO, CO_2.

The Criegee intermediates can decompose to form HO radicals, which are expected to be formed in conjunction with a number of β-oxo alkenyl radicals. Comparatively low HO radical yields in the range 6 % – 10 % have been reported (Shu and Atkinson, 1994; Winterhalter et al., 2009; Jenkin et al., 2012), preferred value 8 ± 3 %. The further chemistry of the β-oxo alkenyl radicals may form a number of reported multifunctional organic products containing hydroxy, carbonyl and acid functionalities (e.g., Calogirou et al., 1997; Jaoui et al., 2003; Kanawati et al., 2008; Winterhalter et al., 2009; Li et al., 2011), and also formaldehyde, CO and CO_2, which have been reported to be formed with respective molar yields of (7.7 ± 4.0) %, (2.0 ± 1.8) % and (3.8 ± 2.8) % by Winterhalter et al. (2009) from ozonolysis of the more reactive endocyclic double bond.

Products likely to be produced from alternative reactions of the Criegee intermediates (I) and (II) have also been detected. The formation of β-caryophyllon aldehyde and/or β-caryophyllonic acid has been positively identified in a number of studies (e.g., Calogirou et al., 1997; Kanawati et al., 2008; Winterhalter et al., 2009; Li et al., 2011; Jenkin et al., 2012), with respective molar yields of 17.3 % and 13.0 % reported by Jaoui et al. (2003) at ~80% relative humidity, in the absence of an HO scavenger. The theoretical calculations of Nguyen et al. (2009) propose an important role for a thermally-stable secondary ozonide (SOZ), which is potentially formed by ring-closure of either of the Criegee intermediates (I) and (II), and suggest it should be the dominant gas phase ozonolysis product (molar yield $\geq$ 65 %). The experimental

study of Winterhalter et al. (2009) provided some qualitative support for SOZ formation, and established that its yield apparently decreases with increasing relative humidity, consistent with its formation occurring at least partially in competition with the bimolecular reactions of the Criegee intermediates with H_2O. Detection of the multifunctional ester (III), which can potentially be formed from rearrangement of (I) or (II), has also been reported by Kanawati et al. (2008) and Winterhalter et al. (2009). The CIR-TOF-MS product study of Jenkin et al. (2012) also confirmed significant collective formation of SOZ and its isomers β-caryophyllonic acid and the multifunctional ester (III). Further experimental quantification of product yields is clearly required, particularly in relation to formation, stability and further reaction of the secondary ozonide, SOZ.

Winterhalter et al. (2009) also determined an HO yield of (16.4 ± 3.6) % for bulk ozonolysis of the first-generation suite of products containing the originally exocyclic double bond. This was facilitated by their reactivity with O_3 being lower than that of β-caryophyllene by a factor of about 100, allowing temporal separation of the oxidation steps.

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