Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC37

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O_3 + (α-humulene) → products
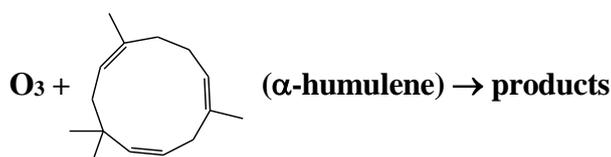
Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(1.12 \pm 0.17) \times 10^{-14}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (a),(b)
$(1.07 \pm 0.08) \times 10^{-14}$	296 ± 2	Shu and Atkinson, 1994	RR-GC (a),(c)
$(2.9 \pm 1.9) \times 10^{-15}$	366 ± 2	Ghalaieny et al., 2012	RR-GC (d)
$(1.28 \pm 0.35) \times 10^{-14}$	295 ± 2	Richters et al., 2015	RR-GC-MS (e)
$(1.43 \pm 0.24) \times 10^{-14}$	295 ± 2	Richters et al., 2015	RR-MS (f)

α-humulene is 2,6,6,9-tetramethyl-1,4-8-cycloundecatriene

Comments

(a) The concentrations of α-humulene and 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, $k(O_3 + \text{α-humulene})/k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = (10.3 \pm 1.6)$ and $k(\text{α-humulene})/k(O_3 + \text{terpinolene}) = (0.564 \pm 0.043)$, are placed on an absolute basis using $k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 296 K; and $k(O_3 + \text{terpinolene}) = 1.6 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendations).
(b) Relative to 2,3-dimethyl-but-2-ene.
(c) Relative to terpinolene.
(d) The concentrations of α-humulene 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, $k(O_3 + \text{α-humulene})/k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 2.2$, is placed on an absolute basis using $k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.32 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} at 366 K (IUPAC, current recommendation). It is noted that the authors used a much lower value of $k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 2.89 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1}, based on a relative rate measurement reported in the same study, leading to a reported value of $k = (6.4 \pm 4.2) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 366 K.
(e) The concentrations of α-humulene 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, $k(O_3 + \alpha\text{-humulene})/k(O_3 + \alpha\text{-terpinene}) = (0.75 \pm 0.04)$, is placed on an absolute basis using $k(O_3 + \alpha\text{-terpinene}) = 1.9 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendation).

(f) The concentrations of α-humulene 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, $k(O_3 + \alpha\text{-humulene})/k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = (11.7 \pm 0.8)$, is placed on an absolute basis using $k(O_3 + 2,3\text{-dimethyl-but-2-ene}) = 1.09 \times 10^{-15}$ 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 relative rate determinations of Shu and Atkinson (1994) and Richters et al. (2015), which are in good agreement. 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 potentially proceeds by initial addition of O_3 to any of the three endocyclic C=C bonds in α-humulene, although there have been no studies from which the attack distribution can be elucidated. Structure-activity methods based on a summation of the rate coefficients for simple alkene structures (e.g. Calvert et al., 2000) suggest that addition at all sites is likely to be competitive, with the methyl-substituted C=C bonds being more favoured. However, such methods also underestimate the observed value of k by an order of magnitude, suggesting a general elevating influence of ring strain on reactivity with O_3. It is therefore not currently possible to draw firm conclusions about the attack distribution of O_3 at the three C=C bonds in α-humulene.

The initial addition of O_3 is expected to form a set of three "primary ozonides", which rapidly decompose via ring-opening to form six carbonyl-substituted Criegee intermediates. The Criegee intermediates can decompose to form HO radicals, which are expected to be formed in conjunction with a number of β-oxo dialkenyl radicals. Comparatively low HO radical yields of $(22\ ^{+11}_{-7})$ % and (10.5 ± 0.7) % have been reported by Shu and Atkinson (1994) and Beck et al. (2011), respectively. The further chemistry of the β-oxo dialkenyl co-radicals may form a large number of multifunctional organic products containing hydroxy, carbonyl and acid functionalities, some of which have been reported by Beck et al. (2011); and also formaldehyde and acetone, which have been reported to be formed with respective molar yields of (3.5 ± 1.1) % and (1.2 ± 0.4) % by Lee et al. (2006). Organic products likely to be produced from alternative reactions of the Criegee intermediates (e.g. C$_{15}$ dicarbonyls and oxo-carboxylic acids from the reactions with H$_2$O) have also been detected, in addition to one or more "secondary ozonides" formed by intramolecular ring-closure of the Criegee intermediates (Beck et al., 2011).

Beck et al. (2011) also characterized the bulk reactivity of O_3 with the suites of first-generation products (containing two C=C bonds) and second generation products (containing one C=C bond), which

were found to be lower than that of α-humulene by respective factors of about 30 and 400. The temporal separation of the oxidation steps allowed detected products to be attributed to the different generations of oxidation. An HO yield of (12.9 ± 0.7) % was also determined for bulk ozonolysis of the first-generation suite of products.

References

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