Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC22

$O_3 +$ (2-carene) $\rightarrow$ products
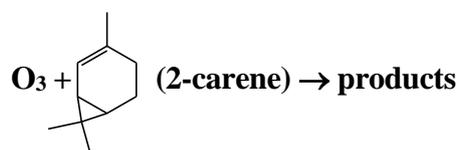
Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.32 \pm 0.30) \times 10^{-16}$	296 ± 2	Atkinson et al., 1990	S-CL/GC (a)
Relative Rate Coefficients			
$(2.56 \pm 0.27) \times 10^{-16}$	296 ± 2	Atkinson et al., 1990	RR-GC (b)

2-carene is 3,7,7-trimethyl-bicyclo[4.1.0]hept-2-ene

Comments

(a) k determined from the observed first-order rate of ozone decay (measured with a chemiluminescence analyzer) in the presence of known excess concentrations of 2-carene (measured by GC-FID). Experiments were carried out in a 160 L Teflon chamber.

(b) The concentrations of a series of alkenes (including 2-carene and α-pinene, the reference compound), with cyclohexane to scavenge HO radicals, were monitored by GC-FID in a 3600 L Teflon chamber at 740 Torr (990 mbar) pressure of purified air in the presence of O_3. The measured rate coefficient ratio $k(O_3 + 2\text{-carene})/k(O_3 + \alpha\text{-pinene})$ is placed on an absolute basis using $k(O_3 + \alpha\text{-pinene}) = 9.46 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 296 K (IUPAC, current recommendation).

Preferred Values

| Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.4×10^{-16}	298

Reliability

$\Delta \log k$	± 0.20	298

The preferred value of the rate coefficient is the average of the absolute and relative rate coefficients reported by Atkinson et al. (1990), the only study of the kinetics of the reaction to date. Confirmatory studies are required.

There has been only limited product and mechanistic information reported in the literature. Based on general understanding of the reactions of ozone with alkenes and terpenes, the reaction is expected to proceed by initial addition of O_3 to the C=C bond in 2-carene to form a "primary ozonide (POZ)" which rapidly decomposes, mainly to form two carbonyl-substituted Criegee intermediates ((I) and (II)), as represented in the following schematic:
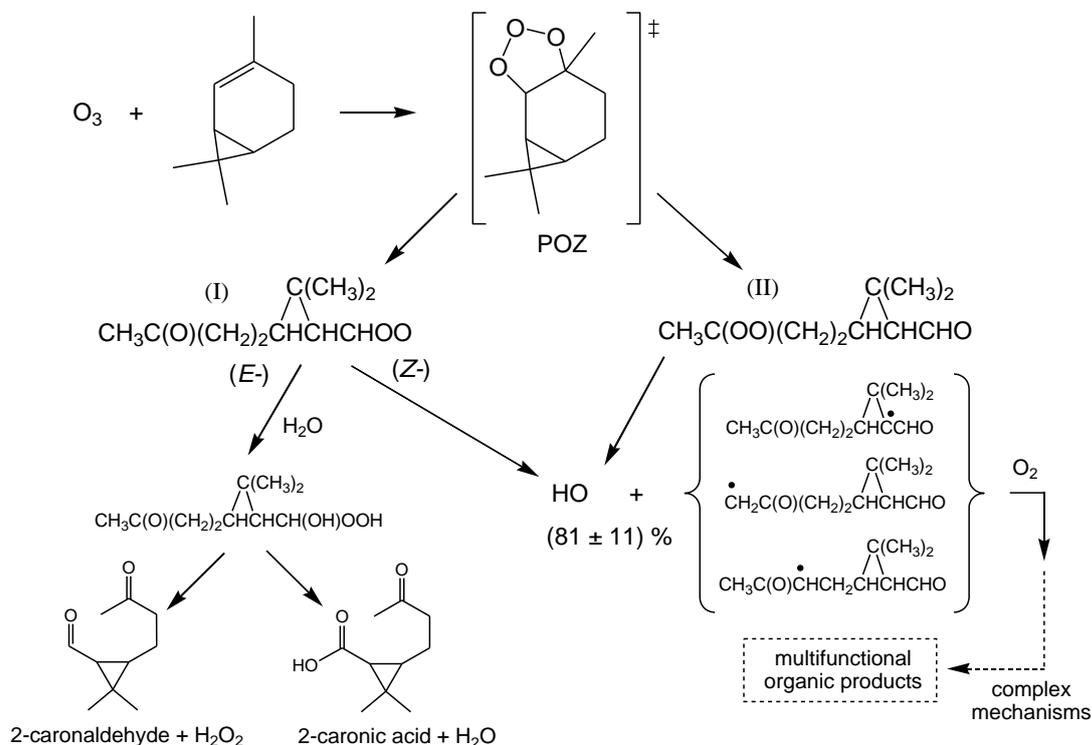
Based on the high reported yield of HO radicals, $(81 \pm 11\ \%)$ (Aschmann et al., 2002), it is likely that the Criegee intermediates mainly decompose to form HO radicals and a number of β-oxo alkyl radicals, as shown above. The further chemistry of the β-oxo alkyl radicals is expected to form a number of multifunctional organic products containing hydroxy, hydroperoxy, carbonyl and acid functionalities, but there have been no reported studies identifying organic products.

Formation of HO via the accepted decomposition mechanism (involving abstraction of a β-hydrogen via a vinyl hydroperoxide intermediate) is not possible for the *E-* conformer of Criegee Intermediate (I) (e.g. see Johnson and Marston, 2008). If stabilized, this is expected to react predominantly with H_2O under atmospheric conditions, leading to the formation of 2-caronaldehyde and H_2O_2, or 2-caronic acid. Some support for this comes from the significant yield ($\approx 18\ \%$) of H_2O_2 from 2-carene ozonolysis at close to 100 % relative humidity (Hewitt and Kok, 1991).

References

Aschmann, S. M., Arey, J. and Atkinson, R.: Atmos. Environ., 36, 4347, 2002.
Atkinson, R., Hasegawa, D. and Aschmann, S. M.: Int. J. Chem. Kinet., 22, 871, 1990.
Hewitt, C. N. and Kok, G. L.: J. Atmos. Chem., 12, 181, 1991.
Johnson, D. and Marston, G.: Chem. Soc. Rev., 37, 699, 2008.