Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC40

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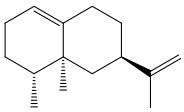
O_3 +  **(valencene) → products**

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Relative Rate Coefficients			
(4.95 ± 1.23) x 10^{-17}	297 ± 3	Ham, 2013	GC-MS (a),(b)
(1.25 ± 0.32) x 10^{-16}	297 ± 3	Ham, 2013	RR-MS (a),(c)

valencene is (3R,4aS,5R)-3-isopropenyl-4a,5-dimethyl-1,2,3,4,4a,5,6,7-octahydronaphthalene

Comments

(a) The concentrations of valencene and 3-carene or γ-terpinene (the reference compounds) were monitored by GC-FID in a 100 L Teflon chamber in purified air in the presence of O_3. The measured rate coefficient ratios $k(O_3 + \text{valencene})/k(O_3 + \text{3-carene}) = (1.01 \pm 0.25)$ and $k(O_3 + \text{valencene})/k(O_3 + \gamma\text{-terpinene}) = (0.78 \pm 0.20)$ are placed on an absolute basis using $k(O_3 + \text{3-carene}) = 4.9 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} and $k(O_3 + \gamma\text{-terpinene}) = 1.6 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} (IUPAC, current recommendations).
(b) Relative to 3-carene.
(c) Relative to γ-terpinene.

Preferred Values

No recommendation

Comments on Preferred Values

The sole investigation of Ham (2013) provides evidence that the reaction of O_3 with valencene occurs, and that k is likely sufficiently high that the reaction will contribute to valencene removal under atmospheric conditions. However, the level of disagreement in the two reported determinations, and inevitable complications arising from not scavenging HO radicals in the system, preclude recommendation of a preferred value. Further kinetics studies are required.

The reaction is expected to proceed via addition of O_3 to both the endocyclic and exocyclic C=C bonds in valencene, with the subsequent mechanism following the general framework outlined in the datasheets for other mono- and sesquiterpenes. However, there have apparently been no product or mechanistic studies to confirm this.

References

Ham, J. E: Int. J. Chem. Kinet., 45, 508 2013.