IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet Ox_VOC14

This data sheet last evaluated : 30th July 2007; no revision of preferred values.

$O_3 + (CH_3)_2C(OH)CH=CH_2 \rightarrow$ products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(1.00 \pm 0.03) \times 10^{-17}$	291 ± 1	Grosjean and Grosjean, 1994	S-UV
$(8.3 \pm 1.0) \times 10^{-18}$	293 ± 2 K	Klawatsch-Carrasco et al., 2004	S-FTIR
Relative Rate Coefficients			
9×10^{-18}	298 ± 2	Fantechi et al., 1998a	RR (a)

Comments

(a) O_3 was reacted with 2-methyl-3-buten-2-ol and propene or 2-methylpropene (the reference compounds) in the presence of propane as an HO radical scavenger. The concentrations of 2-methyl-3-buten-2-ol and propene or 2-methylpropene were monitored by FTIR spectroscopy. The measured rate coefficient ratios (which were not reported) were placed on an absolute basis by use of rate coefficients at 298 K of $k(O_3 + \text{propene}) = 1.2 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} (Atkinson et al., 1992) and $k(O_3 + \text{2-methylpropene}) = 1.13 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} (Atkinson, 1997). The reference compound corresponding to each of the two reported rate coefficients of $k(O_3 + \text{2-methyl-3-buten-2-ol}) = (1.15 \pm 0.22) \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} and $(8.0 \pm 1.0) \times 10^{-18}$ cm^3 molecule^{-1} s^{-1} was not reported; however, using the currently recommended rate coefficients at 298 K of $k(O_3 + \text{propene}) = 1.01 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003; IUPAC, current recommendation) and $k(O_3 + \text{2-methylpropene}) = 1.13 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} (Atkinson and Arey, 2003) results in the approximate average rate coefficient cited in the table.

Preferred Values

$k = 1.0 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The rate coefficients of Grosjean and Grosjean (1994), Fantechi et al. (1998a) and Klawatsch-Carrasco et al. (2004) are in reasonable agreement. However, as noted in comment (a), the lack of detail in the Fantechi et al. (1998a) publication makes re-evaluation of their data somewhat uncertain, especially the derivation of the associated uncertainty. Assuming that the reaction of O_3 with 2-methyl-3-buten-2-ol has a similar temperature dependence to the reactions of O_3 with propene and 2-methylpropene [which have similar room temperature rate coefficients as noted in comment (a)], then the Grosjean and Grosjean (1994) and Klawatsch-Carrasco et al. (2004) rate coefficients correspond to 298 K rate coefficients of 1.16×10^{-17} cm^3 molecule^{-1} s^{-1} and 9.2×10^{-18}

cm^3 $molecule^{-1}$ s^{-1}. The preferred value is an average of the 298 K rate coefficients obtained from the studies of Grosjean and Grosjean (1994), Fantechi et al. (1998a) and Klawatsch-Carrasco et al. (2004).

The reaction proceeds by initial addition of O_3 across the C=C bond to form a "primary ozonide" which rapidly decomposes to $(CH_3)_2C(OH)CHO + [CH_2OO]^*$ or $HCHO + [(CH_3)_2C(OH)CHOO]^*$ (Grosjean and Grosjean, 1995; Fantechi et al., 1998b; Alvarado et al., 1999; Carrasco et al., 2007). Product studies of this reaction have been carried out by Grosjean and Grosjean (1995), Fantechi et al. (1998b), Alvarado et al. (1999) and Carrasco et al. (2007), and the observed products are HCHO, $(CH_3)_2C(OH)CHO$ (2-hydroxy-2-methylpropanal), acetone, formic acid, formic anhydride and HO radicals. There are significant discrepancies in the measured yields of formaldehyde, 2-hydroxy-2-methylpropanal and acetone (Grosjean and Grosjean, 1995; Fantechi et al., 1998b; Alvarado et al., 1999; Carrasco et al., 2007), with the recent study of Carrasco et al. (2007) showing that the yields of acetone and 2-hydroxy-2-methylpropanal depend on the water vapor concentration. Alvarado et al. (1999) reported that at ~5% relative humidity at 298 ± 2 K, the molar formation yields were: HCHO, 29 ± 3%; $(CH_3)_2C(OH)CHO$, ~47%; acetone, initially ~15% and apparently increasing with the extent of reaction; and OH radicals, 19^{+10}_{-7}%. As discussed by Grosjean and Grosjean (1995) and Alvarado et al. (1999), acetone is presumably formed from the $[(CH_3)_2C(OH)CHOO]^*$ Criegee intermediate, and this may account for the variable yields reported (Grosjean and Grosjean, 1995; Fantechi et al., 1998b; Alvarado et al., 1999) and for the observation of Alvarado et al. (1999) of an increasing yield with extent of reaction. Carraso et al. (2007) had available a synthesized sample of 2-hydroxy-2-methylpropanal and carried out experiments under dry conditions and at 20% and 30% relative humidity at 298 ± 2 K. In dry air, the HCHO, $(CH_3)_2C(OH)CHO$ and acetone yields were 44 ± 5%, 43 ± 12% and 39 ± 22%, respectively, while at 20-30% relative humidity the respective formation yields were 55 ± 3%, 84 ± 8%, and acetone was not detected (Carrasco et al., 2007). The product data indicate that the $[(CH_3)_2C(OH)CHOO]^*$ Criegee intermediate is the source of acetone under dry conditions (or at low water vapor concentrations), while at higher water vapor concentrations $[(CH_3)_2C(OH)CHOO]^*$ reacts with water vapor to form $(CH_3)_2C(OH)CHO$ (Carrasco et al., 2007). While there are still some unresolved differences between the various studies, it appears that the reaction initially forms $(CH_3)_2C(OH)CHO + [CH_2OO]^*$ and $HCHO + [(CH_3)_2C(OH)CHOO]^*$ in approximately equal amounts, with the $[(CH_3)_2C(OH)CHOO]^*$ Criegee intermediate reacting to form at least part of the HO radicals observed (Alvarado et al., 1999) and also reacting with water vapor (when present) to form additional $(CH_3)_2C(OH)CHO$.

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