Electronic Supplementary Material for PCCP

RATE CONSTANTS FOR THE GAS-PHASE REACTIONS OF OH RADICALS WITH *E*-7-TETRADECENE, 2-METHYL-1-TRIDECENE AND THE C_7-C_{14} 1-ALKENES AT 295 ± 1 K

Supplementary Material

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For the alkenes studied here, the estimation method of Kwok and Atkinson[1] treats OH radical addition to C=C bonds and H-atom abstraction from CH_2 and CH_3 groups as separate, additive processes. H-atom abstraction from vinylic C-H bonds is assumed to be negligible. Rate constants for OH radical addition to $RCH=CH_2$, $RR'C=CH_2$, *Z*- RCH=CHR' and *E*-RCH=CHR' systems (R, R' = alkyl) are taken to be equal to those for the reactions of OH radicals with propene, 2-methylpropene, *Z*-2-butene and *E*-2-butene, respectively, with rate constants at 298 K of k_{add} (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) of 26.3, 51.4, 56.1 and 64.0, respectively.[1] H-atom abstraction from CH_2 and CH_3 groups is calculated using rate constants k_{sec} and k_{prim}, respectively, combined with substituent group factors, *F*(X). H atom abstraction from a CH_3 group bonded to group X is given by $k_{abstr}(CH_3\text{-}X) = k_{prim}F(X)$, and from a CH_2 group bonded to groups X and Y is given by $k_{abstr}(X\text{-}CH_2\text{-}Y) = k_{sec}F(X)F(Y)$, where the values of k_{prim} and k_{sec} and the group substituent factors *F*(X) and *F*(Y) were derived from the kinetic data for alkanes.[1] At 298 K, $k_{prim} = 1.36 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, $k_{sec} = 9.34 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, $F(CH_3) = 1.00$ (by definition), $F(CH_2) = 1.23$, and $F(>C=C<) \sim 1.0$.[1] As an example, the ate constant for the reaction of OH radicals with 1-decene, $CH_2=CHCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, is given by $k_{total} = k_{addition} + k_{abstraction} = k_{add}(RCH=CH_2) + k_{sec}F(>C=C<)F(CH_2) + 5k_{sec}F(CH_2)F(CH_2) + k_{sec}F(CH_2)F(CH_3) + k_{prim}F(CH_2) = \{26.3 + (0.934 \times 1.0 \times 1.23) + (5 \times 0.934 \times 1.23 \times 1.23) + (0.934 \times 1.0 \times 1.23) + (0.136 \times 1.23)\} \times 10^{-12} = 35.8 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} at 298 K.

References

(1) E. S. C. Kwok and R. Atkinson, *Atmos. Environ.*, 1995, **29**, 1685-1695.