IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HOx_VOC76

This data sheet last evaluated: June 2016; last change in preferred values: June 2016.

HO + $C_2H_5CH(OH)CHO$ → $C_2H_5CH(OH)CO$ (1)
HO + $C_2H_5CH(OH)CHO$ → $C_2H_5C(OH)CHO$ (2)

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	T/K	Reference	Technique/ Comments
Relative Rate Coefficients			
$(2.37 \pm 0.23) \times 10^{-11}$	296 ± 2	Baker et al., 2004	RR-GC (a, b)

Comments

(a) HO radicals were generated by the photolysis of CH_3ONO-NO-air mixtures at 986 mbar (740 Torr) total pressure of purified air at > 300 nm. Experiments were carried out in a 7500 liter Teflon chamber. 2-hydroxybutanal was generated in situ from the OH radical-initiated reaction of 1,2-butanediol. The concentrations of 2-hydroxybutanal and its precursor, 1,2-butanediol, were measured by gas chromatography. From comparison of the measured time-concentration behaviour of $C_2H_5CH(OH)CHO$ and its precursor with calculations a rate coefficient ratio of k(HO + 2-hydroxybutanal)/k(HO + 1,2-butanediol) = 0.944 ± 0.074 was derived. This rate coefficient ratio is placed on an absolute basis using k(HO + 1,2-butanediol) = 2.51×10^{-11} cm^3 molecule^{-1} s^{-1} (Calvert et al., 2011).

(b) Relative to HO + 1,2-butanediol.

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	2.4×10^{-11}	298
Reliability		
$\Delta \log k$	± 0.1	298

Comments on Preferred Value

The recommendation is based upon the relative study by Baker et al. (2004). The possible channels for reaction of $C_2H_5CH(OH)CHO$ with OH are:

$$HO + CH_3CH_2CH(OH)CHO \rightarrow CH_3CH_2CH(OH)CO + H_2O \quad (1)$$
$$\rightarrow CH_3CH_2C(OH)CHO + H_2O \quad (2)$$
$$\rightarrow CH_3CHCH(OH)CHO + H_2O \quad (3)$$
$$\rightarrow CH_2CH_2CH(OH)CHO + H_2O \quad (4)$$
$$\rightarrow CH_3CH_2CH(O)CHO + H_2O \quad (5)$$

The channels (3), (4) and (5) are expected to be of minor importance compared to the channels (1) and (2). Hence, the reaction is expected to proceed mainly via abstraction of the aldehydic hydrogen to give $C_2H_5CH(OH)CO$ radicals (channel (1)) and through the H-atom abstraction from the >CH- group in the α-position to the hydroxyl group leading to $C_2H_5C(OH)CHO$ radicals (channel (2)) similarly to the reaction of OH with hydroxyacetaldehyde ($HOCH_2CHO$).

References

Baker, J., Arey, J., and Atkinson, R.: J. Phys. Chem. A, 108, 7032, 2004.
Calvert, J. G., Mellouki, A., Orlando, J. J., Pilling, M. J., and Wallington T. J.: The Mechanisms of Atmospheric Oxidation of the Oxygenates, Oxford University Press, New York, NY, 2011.