

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC33

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This data sheet last evaluated: 30th July 2007; revision of preferred values.

HO + (CH₃)₂C(OH)CHO → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
(1.49 ± 0.21) × 10 ⁻¹¹	296 ± 2	Baker et al., 2004	RR (a)
(1.36 ± 0.14) × 10 ⁻¹¹	295 ± 2	Carrasco et al., 2006	RR (b)
(1.23 ± 0.06) × 10 ⁻¹¹	293 ± 2	Carrasco et al., 2006	RR (c)

Comments

- (a) HO radicals were generated by the photolysis of CH₃ONO-NO-air mixtures at wavelengths >300 nm. (CH₃)₂C(OH)CHO was generated in situ from the reaction of HO radicals with (CH₃)₂C(OH)CH=CH₂ and its concentration was measured during the reactions using solid phase microextraction fibers pre-coated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine for on-fiber derivatization of carbonyl compounds, with subsequent GC analyses. From the time-concentration behavior of (CH₃)₂C(OH)CHO during the reactions, the rate coefficient ratio $k(\text{HO} + (\text{CH}_3)_2\text{C}(\text{OH})\text{CHO})/k(\text{HO} + (\text{CH}_3)_2\text{C}(\text{OH})\text{CH}=\text{CH}_2) = 0.234 \pm 0.033$ was derived. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient at 296 K of $k(\text{HO} + (\text{CH}_3)_2\text{C}(\text{OH})\text{CH}=\text{CH}_2) = 6.36 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2007).
- (b) HO radicals were generated by the photolysis of HONO at ~420 nm in synthetic air at atmospheric pressure. A synthesized sample of (CH₃)₂C(OH)CHO was used, and the concentrations of (CH₃)₂C(OH)CHO and isoprene (the reference compound) were monitored by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + (\text{CH}_3)_2\text{C}(\text{OH})\text{CHO})/k(\text{HO} + \text{isoprene}) = 0.135 \pm 0.014$ is placed on an absolute basis by use of a rate coefficient at 296 K of $k(\text{HO} + \text{isoprene}) = 1.01 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, 2007).
- (c) HO radicals were generated by the photolysis of H₂O₂ in air by natural sunlight in the EUPHORE chamber at atmospheric pressure. A synthesized sample of (CH₃)₂C(OH)CHO was used, and the concentrations of (CH₃)₂C(OH)CHO and di-*n*-butyl ether (the reference compound) were monitored by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + (\text{CH}_3)_2\text{C}(\text{OH})\text{CHO})/k(\text{HO} + \text{di-}n\text{-butyl ether}) = 0.43 \pm 0.02$ is placed on an absolute basis by use of a rate coefficient at 293 K of $k(\text{HO} + \text{di-}n\text{-butyl ether}) = 2.87 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Mellouki et al., 1995).

Preferred Values

$$k = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

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

Comments on Preferred Values

The two kinetic studies of this reaction are in good agreement, and the preferred value is the average of the three measurements, all of which are relative rate measurements using different reference compounds. Product studies show that acetone is formed in essentially 100% yield in both the presence and absence of NO, with molar yields of 1.06 ± 0.06 in the presence of NO and 1.10 ± 0.06 in the absence of NO (Carrasco et al., 2006). The reaction is expected to proceed mainly by H-atom abstraction from the –CHO group (Baker et al., 2004; Carrasco et al., 2006).

References

- Baker, J., Arey, J. and Atkinson, R.: *J. Phys. Chem. A*, 108, 7032, 2004.
Carrasco, N., Doussin, J.-F., Picquet-Varrault, B. and Carlier, P.: *Atmos. Environ.* 40, 2011, 2006.
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Mellouki, A., Teton, S., Le Bras, G.: *Int. J. Chem. Kinet.* 27, 791, 1995.