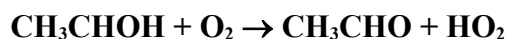


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet R_Oxygen_13

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This data sheet updated: 12th June 2003.



$$\Delta H^\circ = -87.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$\{1.4 \times 10^{-8} T^{-1.2} + 8.0 \times 10^{-10} \exp(-2525/T)\}$	300-682	Grotheer <i>et al.</i> , 1988 ¹	DF-MS (a)
1.56×10^{-11}	300		
$(1.3 \pm 0.2) \times 10^{-11}$	300	Anastasi <i>et al.</i> , 1989 ²	PR-AS (b)
$(2.8 \pm 0.2) \times 10^{-11}$	293	Miyoshi, Matsui and Washida, 1989 ³	PLP-MS (c)

Comments

- CH₃CHOH was generated from Cl + C₂H₅OH in the presence of a large excess of O₂ at total pressures of ~1 mbar (~0.8 Torr). The rate coefficient k was derived from the disappearance of CH₃CHOH, as monitored by low electron energy MS.
- Pulsed radiolysis of Ar-SF₆-HCl-C₂H₅OH-O₂ mixtures at total pressures of 1 bar (760 Torr) and with [SF₆] >> [HCl] >> [C₂H₅OH] >> [O₂]. CH₃CHOH was generated from Cl + C₂H₅OH and monitored by UV absorption at 260 nm.
- Pulsed laser photolysis of CH₃COCHOHCH₃ in a large excess of He at total pressures of 2.7 mbar to 9.3 mbar (2 Torr to 7 Torr). CH₃CHOH was monitored by photoionization MS in the presence of excess O₂.

Preferred Values

$$k = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value of k_{298} is the mean of the results of Grotheer *et al.*,¹ Anastasi *et al.*² and Miyoshi *et al.*³ The rather large discrepancy between the data of Miyoshi *et al.*³ and the other two studies^{1,2} could be due to the different sources of generation of the CH₃CHOH radical. CH₃CHOH radical generation^{1,2} involving Cl attack on C₂H₅OH may not be as clean a source as is the photolysis³ of CH₃COCHOHCH₃.

The temperature dependence of the rate coefficient determined by Grotheer *et al.*¹ shows a marked non-Arrhenius behavior, but this needs to be confirmed before a recommendation can

be made. Evidence for the reaction between CH_3CHOH and O_2 yielding CH_3CHO as a major product comes from the product study of the photooxidation of ethanol by Carter *et al.*⁴

References

- ¹ H.-H. Grotheer, G. Riekert, D. Walter, and Th. Just, 22nd International Symposium on Combustion, 1988 (Combustion Institute, Pittsburgh, PA, 1989), pp. 963-972.
- ² C. Anastasi, V. Simpson, J. Munk, and P. Pagsberg, Chem. Phys. Lett. **164**, 18 (1989).
- ³ A. Miyoshi, H. Matsui, and N. Washida, Chem. Phys. Lett. **160**, 291 (1989).
- ⁴ W. P. L. Carter, K. R. Darnall, R. A. Graham, A. M. Winer, and J. N. Pitts, Jr., J. Phys. Chem. **83**, 2305 (1979).