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

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$CH_3CHOH + O_2 \rightarrow CH_3CHO + HO_2$

$\Delta H° = -87.6$ kJ·mol^{-1}

Rate coefficient data

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

Comments

(a) CH_3CHOH was generated from Cl + C_2H_5OH in the presence of a large excess of O_2 at total pressures of ~1 mbar (~0.8 Torr). The rate coefficient k was derived from the disappearance of CH_3CHOH, as monitored by low electron energy MS.

(b) Pulsed radiolysis of Ar-SF_6-HCl-C_2H_5OH-O_2 mixtures at total pressures of 1 bar (760 Torr) and with $[SF_6] >> [HCl] >> [C_2H_5OH] >> [O_2]$. CH_3CHOH was generated from Cl + C_2H_5OH and monitored by UV absorption at 260 nm.

(c) Pulsed laser photolysis of $CH_3COCHOHCH_3$ in a large excess of He at total pressures of 2.7 mbar to 9.3 mbar (2 Torr to 7 Torr). CH_3CHOH was monitored by photoionization MS in the presence of excess O_2.

Preferred Values

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

Reliability

$\Delta \log k = \pm 0.3$ at 298 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 CH_3CHOH radical. CH_3CHOH radical generation[1,2] involving Cl attack on C_2H_5OH may not be as clean a source as is the photolysis[3] of $CH_3COCHOHCH_3$.

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).