IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet R_Oxygen_9

Website: http://iupac.pole-ether.fr. See website for latest evaluated data. Data sheets can be downloaded for personal use only and must not be retransmitted or disseminated either electronically or in hardcopy without explicit written permission.

This data sheet last evaluated: November 2007; last change in preferred values: November 2006.

$$CH_3C(O)CH_2 + O_2 + M \rightarrow CH_3C(O)CH_2O_2 + M$$
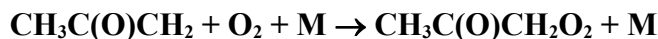
High-pressure rate coefficients

Rate coefficient data

k_∞/cm³ molecule⁻¹ s⁻¹	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
1.45×10^{-12} (1013 mbar, SF_6)	298	Cox et al., 1990	PR-AS (a)
$(9.3 \pm 1.3) \times 10^{-13}$ (444 mbar, He)	298 ± 5	Oguchi et al., 2001	PLP-LIF (b)
$(3.5 \pm 0.5) \times 10^{-13}$ (2.3 mbar, He)	298 ± 1	Imrik et al., 2004	DF-LIF (c)
$(1.18 \pm 0.04) \times 10^{-12}$ (42 mbar, He)	298	Hassouna et al., 2006	PLP-LIF (d)
$7.2 \times 10^{-13} \exp[(131 \pm 27)/T]$	291-520		

Comments

(a) Pulse radiolysis of CH_3COCH_3-O_2-SF_6 mixtures at 1 bar of SF_6. CH_3COCH_2 (acetonyl) radicals were formed from the reaction of F atoms with CH_3COCH_3. At the monitoring wavelength of 310 nm both CH_3COCH_2 and $CH_3COCH_2O_2$ absorb, with the absorption cross-section of the peroxy radical being a factor of 1.7 greater than that of the CH_3COCH_2 radical. The rate coefficient was evaluated by simulations of the above reaction together with the reaction $CH_3COCH_2 + CH_3COCH_2O_2 \rightarrow 2\ CH_3COCH_2O$.

(b) Acetonyl radical was monitored by excitation at 340.6 nm in the pressure range 20.4 to 444 mbar He after pulsed ArF (193 nm) excimer laser photolysis of an alkenylether. Typical radical concentrations were in the range (4-20) x 10^{11} molecule cm⁻³ with a corresponding variation of the second-order rate constant of approximately a factor of two. RRKM calculations revealed a high pressure limiting rate constant $k_\infty = (9.8 \pm 0.8) \times 10^{-13}$ cm³ molecule⁻¹s⁻¹ using an estimated heat of reaction from a G2 level ab initio calculation.

(c) Acetonyl radical was monitored by excitation at 358.7 nm and 2.85 ± 0.05 mbar He total pressure. Acetonyl was generated from H abstraction from acetone by F at a typical concentration of 6 x 10^{11} molecule cm⁻³.

(d) Acetonyl radical was generated by 193 nm photolysis of 2,4-pentanedione and monitored by excitation at 341.6 nm in the pressure range 42 mbar to 10 bar of He in the temperature range 291-520 K. Decays are single exponential for T < 400 K and bi-exponential beyond 400 K owing to dissociation of the O_2-adduct $CH_3COCH_2O_2$. The temperature dependence at 650 mbar comprising data over the full pressure range is thought to correspond to the high-pressure rate constant.

Preferred Values

$k_\infty = 1.2 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

$k_\infty = 7.2 \times 10^{-13} \exp (130/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 300 K.

$\Delta(E/R) = \pm 50$ K

Comments on Preferred Values

The preferred values are based on the arithmetic mean of the results of Cox et al. (1990) and of Oguchi et al. (2001). Hassouna et al. (2006) measure a pressure-independent rate-constant across the whole pressure range at ambient temperature and conclude that the high-pressure limit is reached at 42 mbar in apparent contradiction to Oguchi et al. (2001) who observe a pressure dependence of the rate constant across the entire range (20-444 mbar). The preferred value of k at 298 K does not change when the ambient temperature results of Hassouna et al. (2006) are taken into account as their value is numerically equal to the mean obtained by Cox et al. (1990) and Oguchi et al. (2001). The high-temperature decays observed by Hassouna et al. (2006) at T > 400 K were used to obtain an equilibrium constant in addition to the forward rate constant whose temperature dependence yields $\Delta H_r = -105 \pm 2.0$ kJ mol^{-1} and $\Delta S_r = -143.0 \pm 4.0$ kJ mol^{-1} K for reaction with O_2. This puts a thermodynamic constraint to the theoretical values of the standard heats of formation and the entropy for both 1-methylvinoxy (acetonyl) radical and its O_2-adduct $CH_3COCH_2O_2$ (acetonylperoxyl radical). The recommended value from a combination of an *ab initio* calculation (G3MP2B3) and the Hassouna et al. (2006) data yield $\Delta H^0_f = -32.9$ kJ mol^{-1} for 1-methylvinoxy radical which is within two kJ mol^{-1} of both, theoretical (Hassouna et al., 2006) and experimental (Bouchoux et al., 2001), values.

References

Bouchoux, G., Chamot-Rooke, J., Leblanc, D., Mourgues, P. and Sablier, M.: ChemPhysChem 2, 235, 2001.

Cox, R. A., Munk, J., Nielsen, O. J., Pagsberg, P., and Ratajczak, E.: Chem. Phys. Lett. 173, 206, 1990.

Hassouna, M., Delbos, E., Devolder, P., Viskolcz, B. and Fittschen, Ch.: J. Phys. Chem. A 110, 6667, 2006.

Imrik, K., Farkas, E.; Vasvari, G., Szilagyi, I., Sarzynski, D., Dobé, S., Berces, T. and Marta, F.: Phys. Chem. Chem. Phys. 6, 3958, 2004.

Oguchi, T., Miyoshi, A., Koshi, M., Matsui, H. and Washida, N.: J. Phys. Chem. A, 105, 378, 2001.