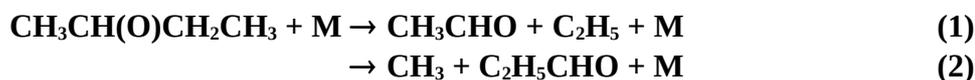


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet RO\_10

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 updated: 16<sup>th</sup> November 2006.



$$\Delta H^\circ(1) = 24.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = 28.5 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = (3.5 \pm 2) \times 10^3$ , 50 mbar $\text{N}_2$	293	Hein et al., 1998	PLP-AS/LIF (a)
$k_\infty = 1.1 \times 10^{14} \exp(-6450/T)$	291-348	Falgayrac et al., 2004	PLP/LIF (b)
$k_0 = 3.2 \times 10^{-8} \exp(-4320/T)$			
$k = 2.9 \times 10^4$ (1 bar)	298		
<i>Relative Rate Coefficients</i>			
$k_1 = 6.3 \times 10^{14} \exp(-7700/T)$	440-471	Batt and McCulloch, 1976 <sup>2</sup>	S-GC (c)
$k_1 = 3.8 \times 10^3$	298*		
$k_1 = 2.2 \times 10^4$	303	Carter et al., 1979	S-GC (d)
$k_1 = 1.95 \times 10^4$	296	Cox et al., 1981	S-GC (e)
$k_1 = 6.3 \times 10^{13} \exp(-7600/T)$	363-503	Heiss et al., 1991	F-TLC/ HPLC (f)
$k_1 = 5.3 \times 10^2$	298*		
$k_1 = 3.9 \times 10^{12} \exp(-5667/T)$	280-313	Libuda et al., 2002	S-FTIR (g), (h)
$k_1 = 2.1 \times 10^4$	298		
$k_1 = 2.2 \times 10^4$	298	Meunier et al, 2003	S-FTIR (i), (h)
$k_1 = 8.1 \times 10^{12} \exp(-5904 \pm 337/T)$	256-310	Cassanelli et al., 2005	FR-GC (j), (h)
$k_1 = 2.0 \times 10^4$	298		
<i>Branching Ratios</i>			
$k_1/k_2 = 0.59 \exp(1350/T)$	399-493	Drew et al., 1985	S-GC (k)
$k_1/k_2 = 55$	298		

### Comments

- (a) Pulsed laser photolysis at 193 or 248 nm of a mixture of 2-bromobutane,  $\text{O}_2$  and  $\text{NO}$  in  $\text{N}_2$  at 50 mbar total pressure in a slow-flow system.  $\text{OH}$  and  $\text{NO}_2$  were monitored in real-time using laser long-path absorption at 308.417 nm and cw laser-excited fluorescence after excitation at 488 nm, respectively. The rate coefficient was derived from a computer simulation of the  $\text{OH}$  and  $\text{NO}_2$  temporal concentration profiles and is in the fall-off region at the total pressure used.
- (b) Laser Photolysis (351 nm) of 2- $\text{C}_4\text{H}_9\text{NO}$ -He mixtures; LIF detection of 2-butoxy radicals. The temperature and pressure dependence of the unimolecular decomposition was measured at total pressures between  $0.01 < p < 0.8$  bar of helium and at four temperatures between 291–348 K. The low and the high pressure limiting rate constants as well as the broadening factor  $F_{\text{cent}}$  have been extracted from a falloff analysis of the experimental results:  $k_{0,\text{He}} = 3.2 \times$

$10^{-8} \exp(-35.9 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ s}^{-1}$ ,  $k_{\infty} = 1.1 \times 10^{14} \exp(-53.6 \text{ kJ mol}^{-1}/RT) \text{ s}^{-1}$ , and  $F_c = 0.87 - T/870 \text{ K}$ . The rate constant at 1 bar, 298 K was calculated from these expressions and led to  $k_1 = 6.7 \times 10^{12} \exp(-5738/T)$ . An uncertainty of  $\pm 30\%$  was estimated for these rate constants which justified setting  $k = k_1$ .

- (c) Pyrolysis of 2-butyl nitrite in the presence of NO at pressures of  $\sim 1$  bar ( $\sim 760$  Torr) in a static system. End-product analysis of  $\text{CH}_3\text{CHO}$  by GC. Results were derived relative to the reaction  $2\text{-C}_4\text{H}_9\text{O} + \text{NO} \rightarrow 2\text{-C}_4\text{H}_9\text{ONO}$  for which a value of  $k = 4.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was taken, independent of temperature.
- (d) Smog chamber photolysis of  $n\text{-C}_4\text{H}_{10}\text{-NO}_x$ -air mixtures at 1 bar pressure. End-product analysis of  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COC}_2\text{H}_5$  by GC yielded  $k_1/k(2\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = 3.15 \times 10^{18} \text{ molecule cm}^{-3}$ . The above value of  $k_1$  was obtained taking  $k = 7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reference reaction  $2\text{-C}_4\text{H}_9\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{COC}_2\text{H}_5 + \text{HO}_2$  (see this evaluation).
- (e) Similar experiments as in comment (b) with  $n\text{-C}_4\text{H}_{10}\text{-HONO}$ -air mixtures yielding  $k_1/k(2\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = (2.60 \pm 0.35) \times 10^{18} \text{ molecule cm}^{-3}$ . The above value of  $k_1$  was obtained taking  $k = 7.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the reference reaction  $2\text{-C}_4\text{H}_9\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{COC}_2\text{H}_5 + \text{HO}_2$  (see this evaluation).
- (f) Pyrolysis of  $(2\text{-C}_4\text{H}_7\text{O})_2$  in a stream of  $\text{O}_2\text{-N}_2$  with end-product analyses. Rate data derived from a computer simulation of yields of  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COC}_2\text{H}_5$  and assuming that  $k = 2.6 \times 10^{-14} \exp(-100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  for the competing reaction  $2\text{-C}_4\text{H}_9\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{COC}_2\text{H}_5 + \text{HO}_2$ .
- (g) Photolysis of  $2\text{-C}_4\text{H}_9\text{I-NO-O}_2\text{-N}_2$  mixtures at 1013 mbar (760 Torr) pressure.  $k/k(2\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = (2.0 \pm 0.5) \times 10^{26} \exp(-5463/T) \text{ molecule cm}^{-3}$  was derived from yields of  $\text{C}_3\text{H}_7\text{CHO}$  and  $\text{CH}_3\text{CHO}$  products, measured by calibrated FTIR spectroscopy. The observed  $[\text{O}_2]$  dependence of this ratio was attributed to influence of 6-10% production of 'hot' 2-butoxy produced in the  $\text{RO}_2 + \text{NO}$  reaction. Pressure dependence of  $\sim$  a factor 1.6 increase in ratio observed over range 100-1000 mbar.
- (h) Cited value of the ratio  $k$  refers to the thermally relaxed 1-butoxy and  $k$  (1 bar) is calculated using a rate coefficient of  $k(2\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = 1.5 \times 10^{-14} \exp(-200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson, 1997).
- (i) Photolysis (420 nm) of  $2\text{-C}_4\text{H}_9\text{NO-NO-O}_2\text{-N}_2$  mixtures or  $n\text{-C}_4\text{H}_{10}\text{-HONO(or CH}_3\text{ONO)-NO-O}_2\text{-N}_2$  mixtures at 1013 mbar (760 Torr) pressure. Analysis by FTIR.  $k/k(1\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = (2.9 \pm 0.4) \times 10^{18} \text{ molecule cm}^{-3}$  was derived from  $[\text{O}_2]$ -dependence of yields of  $\text{C}_2\text{H}_5\text{CH(O)CH}_3$  and  $\text{CH}_3\text{CHO}$  products. No chemical activation observed at this wavelength.
- (j) Photolysis (360 nm) of  $2\text{-C}_4\text{H}_9\text{NO-NO-O}_2\text{-N}_2$  mixtures at 1013 mbar (760 Torr) pressure. Analysis by GC.  $k/k(2\text{-C}_4\text{H}_9\text{O} + \text{O}_2) = 5.4 \times 10^{26} \exp\{-(5704 \pm 350)/T\} \text{ molecule cm}^{-3}$  was derived from  $[\text{O}_2]$ -dependence of  $\text{C}_3\text{H}_7\text{CHO}$  and  $\text{CH}_3\text{CHO}$  products. Evidence for the influence of production of 'hot' 2-butoxy produced in the photolysis of  $2\text{-C}_4\text{H}_9\text{NO}$  5% at 283 K; 9% at 298 K). Cited value of the ratio  $k$  refers to the thermally relaxed 2-butoxy.
- (k) Static thermal generation of radicals from  $\text{F} + 2\text{-C}_4\text{H}_9\text{OH}$  with end-product analysis of  $\text{CH}_3\text{CHO}$  and  $\text{C}_2\text{H}_5\text{CHO}$  by GC.

### Preferred Values

$k_1 = 5.7 \times 10^{12} \exp(-5780/T) \text{ s}^{-1}$  over the temperature range 240 to 340 K and 1 bar pressure.  
 $k_1 = 2.1 \times 10^4 \text{ s}^{-1}$  at 298 K and 1 bar pressure.

#### Reliability

$\Delta \log k_1 = \pm 0.3$  at 298 K.

$\Delta(E_i/R) = \pm 500 \text{ K}$ .

#### Comments on Preferred Values

The recent results for the temperature dependence of the relative rate coefficients agree well with the room temperature data of Carter et al. (1979), Cox et al. (1981) and Meunier et al. (2003), especially when the small effects of 'hot' 2-butoxy formation are taken into account. The preferred 298 K value of  $k$  is a mean value based on the measured ratios of  $k/k(2\text{-butoxy} + \text{O}_2)$  of Carter et al. (1979), Cox et al. (1981), Libuda et al. (2002), Meunier et al. (2003) and Cassanelli et al. (2005), using a rate coefficient of  $k(2\text{-butoxy} + \text{O}_2) = 1.5 \times 10^{-14} \exp(-200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  recommended by Atkinson (1997). The temperature-dependence is based on an average activation energy from the studies of Libuda et al. (2002) and Cassanelli et al. (2005), and a pre-exponential factor adjusted to fit the recommended 298 K value.

The recent comprehensive temperature and pressure dependence study of Falgayrac et al. (2004) confirms the earlier indications from measurements of Hein et al. (1998) and Libuda et al. (2002) that decomposition is in the fall-off region below 1 bar. The low and the high pressure limiting rate constants as well as the broadening factor  $F_{\text{cent}}$  extracted from a falloff analysis of their experimental results can be used to calculate rate constants at other pressures. The absolute rate coefficient at 1 bar pressure and 298 K ( $= 2.9 \times 10^4 \text{ s}^{-1}$ ) is consistent with the preferred value above within experimental error. The results are in good agreement with predictions from several theoretical studies of this unimolecular decomposition (Somnitz and Zellner (2000), Méreau et al. (2000) and Fittschen et al. (2000)).

Although the branching ratio ( $k_1/k_2$ ) reported by Drew et al. (1985) seems reasonable, it requires further confirmation before a recommendation can be made. None of the other studies (Batt and McCulloch, 1976; Carter et al., 1979; Cox et al., 1981) of the decomposition of the 2-C<sub>4</sub>H<sub>9</sub>O radicals has reported C<sub>2</sub>H<sub>5</sub>CHO as a product of the decomposition reaction, and it is possible that the radical generation system of Drew et al. (1985) is more complicated than they suggested.

## References

- Atkinson, R., J. Phys. Chem. Ref. Data, 26, 215, 1997; Int. J. Chem. Kinet., 29, 99, 1997.
- Batt, L. and McCulloch, R. D.: Int. J. Chem. Kinet. 8, 911, 1976.
- Carter, W. P. L., Lloyd, A. C., Sprung, J. L., and Pitts, Jr., J. N.: Int. J. Chem. Kinet. 11, 45, 1979.
- Cassanelli, P., Johnson, D. and Cox, R. A.: Phys. Chem. Chem. Phys. 7, 3702, 2005.
- Cox, R. A., Patrick, K. F., and Chant, S. A.: Environ. Sci. Technol. 15, 587, 1981.
- Drew, R. M., Kerr, J. A., and Olive, J.: Int. J. Chem. Kinet. 17, 167, 1985.
- Falgayrac, G., Caralp, F., Sokolowski-Gomez, N., Devolder, P. and Fittschen, C.: Phys. Chem. Chem. Phys., 6, 4127, 2004.
- Fittschen, C., Hippler, H. and Viskolcz, B.: Phys. Chem. Chem. Phys., 2, 1677–1683, 2000.
- Hein, H., Hoffmann, A., and Zellner, R.: Ber. Bunsenges. Phys. Chem. 102, 1840, 1998.
- Heiss, A., Tardieu de Maleissye, J., Viossat, V., Sahetchian, K. A., and Pitts, I. G.: Int. J. Chem. Kinet. 23, 607, 1991.
- Libuda, H. G., Shestakov, O., Theloke, J. and Zabel F.: Phys. Chem. Chem. Phys., 4, 2579-2586, 2002.
- Méreau, R., Rayez, M.-T., Caralp, F. and Rayez, J.-C. : Phys. Chem. Chem. Phys., 2, 3765, 2000.
- Meunier, N., Doussin, J. F., Chevallier, E., Durand-Jolibois, R., Picquet-Varrault, B. and Carlier, P. : Phys. Chem. Chem. Phys. 5, 4834-4839, 2003.
- Somnitz, H. and Zellner, R.: Phys. Chem. Chem. Phys., 2, 1907, 2000.