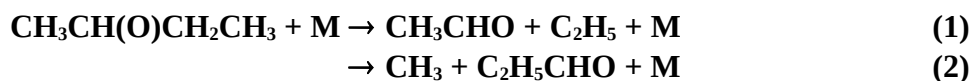


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet RO_10

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This data sheet updated: 16th 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/ s^{-1}	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = (3.5 \pm 2) \times 10^3$, 50 mbar 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 ²	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, O₂ and NO in N₂ at 50 mbar total pressure in a slow-flow system. OH and NO₂ 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 OH and NO₂ temporal concentration profiles and is in the fall-off region at the total pressure used.
- (b) Laser Photolysis (351 nm) of 2-C₄H₉NO-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_{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 ~ 1 bar (~ 760 Torr) in a static system. End-product analysis of CH_3CHO 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 CH_3CHO 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 CH_3CHO 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 CH_3CHO 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 CH_3CHO 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 CH_3CHO 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 CH_3CHO 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.

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

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_{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-C₄H₉O radicals has reported C₂H₅CHO 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.

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