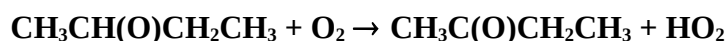


## IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet RO\_9

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



$$\Delta H^\circ = -156.2 \text{ kJ}\cdot\text{mol}^{-1}$$

### Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(6.5 \pm 2.0) \times 10^{-15}$	293	Hein et al., 1998	PLP-AS/LIF (a)
$1.33 \times 10^{-15} \exp(660 \pm 80)/T]$	223-311	Deng et al., 2000	PLP-LIF (b)
$1.2 \times 10^{-14}$	298		
$1.2 \times 10^{-15} \exp(553/T)$	221-266	Deng et al., 2001	PLP/LIF (c)
$7.7 \times 10^{-15}$	298*		
$(9 \pm 3) \times 10^{-15}$	291-295	Falgayrac et al., 2004	PLP-LIF (d)

### Comments

- Pulsed laser photolysis at 193 or 248 nm of a mixture of 2-bromobutane, O<sub>2</sub> and NO in N<sub>2</sub> at 50 mbar total pressure in a slow-flow system. OH and NO<sub>2</sub> 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 NO<sub>2</sub> temporal concentration profiles.
- Pulsed laser photolysis of a mixture of 2-butyl nitrite and O<sub>2</sub> in N<sub>2</sub> at 355 nm at a total pressure in the range 66.5 to 234 mbar (50 to 175 Torr) in a slow flow reactor coupled to fluorescence detection of 2-butoxy radical upon pulsed laser excitation at 365.8 nm. The small negative activation energy is accompanied by an abnormally small A-factor in the rate expression.
- Repeat study as in (b) but with improved experimental arrangement giving less potential problems with secondary chemistry.  $k(298)$  obtained by extrapolation.
- Pulsed laser photolysis of 2-butyl nitrite/O<sub>2</sub> in He at 351 nm coupled to LIF detection of 2-butoxy radical excited near 369 nm in a slow flow reactor. Owing to fast quenching of 2-butoxy radical fluorescence by O<sub>2</sub> only ambient temperature results are reported at 131 mbar.

### Preferred Values

$$k = 7.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.5 \times 10^{-14} \exp(-200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over range } 250\text{-}350 \text{ K.}$$

### Reliability

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

$\Delta(E/R) = \pm 300$  K.

#### *Comments on Preferred Values*

The average of the rate constants of Falgayrac et al. (2004), Hein et al. (1998) and Deng et al. (2001) at ambient temperature is recommended. The negative temperature dependence of  $k$  in the range 223 to 311 K observed by Deng et al. (2000, 2001) could not be confirmed by Falgayrac et al. (2004). The second study of Deng et al. (2001) suggests problems in the earlier study (Deng et al., 2000) while maintaining a small negative activation energy. Although Deng et al. report a negative temperature dependence, we prefer to adopt the temperature dependence estimated by Atkinson (1997), ( $E/R = 200$  K), based on available data for smaller alkoxy radicals, and an A-factor adjusted to give the preferred value at 298 K.

#### **References**

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