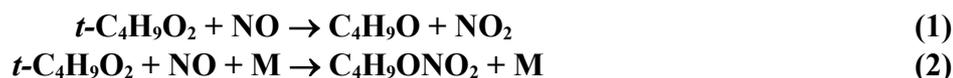


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_37

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. The citation for this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

This data sheet last evaluated: June 2010; last change in preferred values: June 2010.



Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(4.0 \pm 1.1) \times 10^{-12}$	290	Peeters et al., 1992	DF-MS (a)
$(7.9 \pm 1.3) \times 10^{-12}$	297	Eberhard and Howard, 1997	F-CIMS (b)
$(8.6 \pm 1.4) \times 10^{-12}$	298	Xing and Miyoshi, 2005	PLP-MS (c)

Comments

- (a) Fast-flow system with molecular beam sampling MS at a total pressure of 2.7 mbar (2 Torr). $t\text{-C}_4\text{H}_9\text{O}_2$ radicals produced by reaction of O_2 with $t\text{-C}_4\text{H}_9$ radicals produced by thermal decomposition of t -butyl nitrate. $t\text{-C}_4\text{H}_9\text{O}_2$ was detected as its parent negative ion formed by reaction with O_2^- . k was derived from decay of $t\text{-C}_4\text{H}_9\text{O}_2$ in the presence of NO, and appearance of NO_2 .
- (b) Low frequency RF discharge through t -butyl iodide to produce $t\text{-C}_4\text{H}_9$ in the presence of O_2 . $t\text{-C}_4\text{H}_9\text{O}_2$ was detected as its parent negative ion formed by reaction with O_2^- . k determined by pseudo-first order loss of $t\text{-C}_4\text{H}_9\text{O}_2$ in the presence of NO.
- (c) Photolysis of $t\text{-C}_4\text{H}_9\text{Br}$ at 193 nm, or $t\text{-C}_4\text{H}_9\text{I}$ at 248 nm to produce $t\text{-C}_4\text{H}_9$ in the presence of O_2 . $t\text{-C}_4\text{H}_9\text{O}_2$ detected as the negative parent ion following electron transfer from high Rydberg state Xe atoms. The bath gas was 4 – 5.3 mbar (3 – 4 Torr) He. k determined by numerical modelling of the system using a detailed reaction scheme.

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	8.3×10^{-12}	298
<i>Reliability</i>		
$\Delta \log k$	± 0.2	298

Comments on Preferred Values

The preferred value of k is based on the results of Eberhard and Howard (1997) and Xing and Miyoshi (2005), which report values of k which are about a factor of two greater than the earlier determination of Peeters et al. (1992). The preferred value of k is consistent with the wider kinetics database of reactions of NO with hydrocarbon-derived RO₂ radicals, which generally show little sensitivity to the size or structure of the organic group. Studies of the temperature dependence of k are required.

There are currently no reported determinations of the reaction branching ratios, which are generally lacking for tertiary peroxy radicals. Systematic studies as a function of temperature and pressure would be valuable.

References

- Eberhard, J. and Howard, C. J.: J. Phys. Chem. A, 101, 3360, 1997.
Peeters, J., Vertommen, J. and Langhans, I.: Ber. Bunsenges. Phys. Chem., 96, 431, 1992.
Xing, J.-H. and Miyoshi, A.: J. Phys. Chem. A, 109, 4095, 2005.