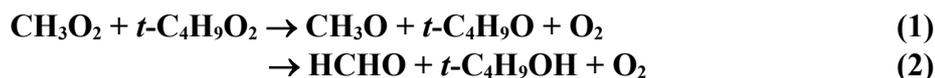


IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_43

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 2011; last change in preferred values: June 2011.



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

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Relative Rate Coefficients</i>			
1.0×10^{-14}	298	Parkes, 1975	UVP-UVA (a)
4.0×10^{-15}	313	Osbourne and Waddington, 1984	UVP-GC (b)
5.8×10^{-15}	343		
1.0×10^{-14}	373		
<i>Branching Ratios</i>			
$k_1/k_2 = 0.5$	298	Parkes, 1975	UVP-UVA (a)
$k_1/k_2 = 1.0$	333	Kirsch and Parkes, 1981	UVP-GC (c)
$k_1/k_2 = 1.7$	373		
$k_1/k_2 = 0.19$	313	Osbourne and Waddington, 1984	UVP-GC (b)
$k_1/k_2 = 0.29$	343		
$k_1/k_2 = 0.50$	393		

Comments

- (a) UV photolysis of $(\text{CH}_3)_2\text{N}_2\text{-O}_2\text{-N}_2$ to generate CH_3O_2 . $(\text{CH}_3)_3\text{CH}$ added to reaction mixtures in large quantities to scavenge CH_3O (formed initially from the CH_3O_2 self reaction), leading to generation of $t\text{-C}_4\text{H}_9\text{O}_2$. k and k_1/k determined from the build up of absorption due to $t\text{-C}_4\text{H}_9\text{O}_2$, using a steady state analysis, with k effectively determined relative to the kinetics of the self-reaction of $t\text{-C}_4\text{H}_9\text{O}_2$.
- (b) UV photolysis of $(t\text{-C}_4\text{H}_9)_2\text{N}_2\text{-O}_2\text{-N}_2$ to generate $t\text{-C}_4\text{H}_9\text{O}_2$, with CH_3O_2 formed as a secondary product following the self reaction of $t\text{-C}_4\text{H}_9\text{O}_2$. Time dependence of the production of $t\text{-C}_4\text{H}_9\text{OH}$, $t\text{-C}_4\text{H}_9\text{OOH}$, acetone and HCHO was characterised as a function of temperature and O_2 concentration. k and branching ratios determined from simulation of the system using a detailed chemical mechanism, with k effectively determined relative to the kinetics of the self-reaction of CH_3O_2 .
- (c) UV photolysis of $(t\text{-C}_4\text{H}_9)_2\text{N}_2\text{-O}_2\text{-N}_2$ to generate $t\text{-C}_4\text{H}_9\text{O}_2$, with CH_3O_2 formed as a secondary product following the self reaction of $t\text{-C}_4\text{H}_9\text{O}_2$. Branching ratios determined from interpretation of the yields of $t\text{-C}_4\text{H}_9\text{OH}$, $t\text{-C}_4\text{H}_9\text{OOH}$ and acetone, obtained as a function of temperature.

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	3.1×10^{-15}	298
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$3.8 \times 10^{-13} \exp(-1430/T)$	298-400
k_1/k	0.13	298
k_2/k	0.87	298
k_1/k	$1/[1 + 4.5 \times 10^{-2} \exp(1490/T)]$	298-400
k_2/k	$1 - (k_1/k)$	298-400
<i>Reliability</i>		
$\Delta \log k$	0.6	298
$\Delta E/R$	$\pm 500 \text{ K}$	
$\Delta k_1/k$	+0.3, -0.1	298
$\Delta k_2/k$	-0.3, +0.1	298
$\Delta(E_1/R - E/R)$	$\pm 500 \text{ K}$	

Comments on Preferred Values

The reported studies of this reaction have all extracted values of k and the branching ratios from the interpretation of product studies of complex systems, and are therefore potentially subject to large uncertainties. Despite this, the results display broadly similar traits, with reported k values of a comparable magnitude, and with k_1/k_2 increasing with temperature. The differences in the derived parameters reflect the uncertainties in the broader chemical mechanism and the applied or assumed parameters used in the interpretation. The preferred values of k and k_1/k are based on the values reported in the most recent study of Osbourne and Waddington (1984), which were obtained from a more detailed appraisal of the chemistry in the system, and included numerical simulations to take explicit account of the impact of secondary reactions. The wide uncertainty limits encompass the results of Parkes (1975) and Kirsch and Parkes (1981). Direct kinetic studies are required to reduce these uncertainty limits.

References

- Kirsch, L.J. and Parkes, D.A.: J. Chem. Soc. Faraday Trans. 1, 77, 298, 1981.
 Osbourne, D.A. and Waddington, D.J.: J. Chem. Soc. Perkin Trans. 2, 1861, 1984.
 Parkes, D.A.: 15th International Symposium on Combustion (The Combustion Institute, Pittsburgh, 1975), p795.

