IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_42

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$$t\text{-}C_4H_9O_2 + t\text{-}C_4H_9O_2 \rightarrow t\text{-}C_4H_9O + t\text{-}C_4H_9O + O_2 \qquad (1)$$
$$\rightarrow t\text{-}C_4H_9OOt\text{-}C_4H_9 + O_2 \qquad (2)$$
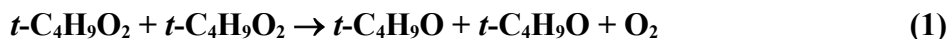
Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$k_{obs} = 2.6 \times 10^{-17}$	295	Parkes, 1975	MM-UVA (a,b)
$k_{obs} = (2.6 \pm 0.8) \times 10^{-17}$	298	Anastasi et al., 1978	FP-UVA (a,c)
$k_{obs} = (8.9 \pm 2.7) \times 10^{-17}$	325		
1.7×10^{-17}	293	Lightfoot et al., 1990	FP-UVA (a,d)
1.0×10^{-11} exp[3894/T]	293-418		

Comments

(a) k is defined by $-d[t\text{-}C_4H_9O_2]/dt = 2k\,[t\text{-}C_4H_9O_2]^2$. k_{obs} denotes an upper limit rate coefficient derived from an experimentally observed decay without correction for probable secondary removal of $t\text{-}C_4H_9O_2$.

(b) UV photolysis of $(t\text{-}C_4H_9)_2N_2\text{-}O_2\text{-}N_2$. The progress of the reaction was followed by time-resolved UV absorption measurements.

(c) UV flash photolysis of $(t\text{-}C_4H_9)_2N_2\text{-}O_2\text{-}N_2$ mixtures. The progress of the reaction was followed by time-resolved UV absorption measurements at 240 nm, close to the maximum of the $t\text{-}C_4H_9O_2$ absorption spectrum, which was also characterised.

(d) $t\text{-}C_4H_9O_2$ generated as a residual product of the propagating channel of the $neo\text{-}C_5H_{11}O_2$ self-reaction, with $neo\text{-}C_5H_{11}O_2$ generated by UV flash photolysis of Cl_2-neopentane-$O_2\text{-}N_2$ mixtures. The much slower removal rate of $t\text{-}C_4H_9O_2$ allowed its self reaction to be investigated after complete decay of $neo\text{-}C_5H_{11}O_2$. The progress of the reaction was followed by time-resolved UV absorption measurements at 240 nm, close to the maximum of the $t\text{-}C_4H_9O_2$ absorption spectrum, yielding: $k_{obs} = 4.6 \times 10^{-11}$ exp[(4233 ± 108)/T]. Values of k were derived from simulations using a 20 reaction mechanism, which took account of secondary removal of $t\text{-}C_4H_9O_2$ through reactions with CH_3O_2 and HO_2. Owing to the sensitivity of the simulations to uncertain parameters, the final expression (given above) was reported to be approximate with no formal error limits assigned.

Preferred Values

Parameter	Value	T/K
$k/$ cm^3 molecule^{-1} s^{-1}	2.1×10^{-17}	298
$k/$ cm^3 molecule^{-1} s^{-1}	1.0×10^{-11} exp (-3900/T)	290-420
k_1/k	1.0	290-420
Reliability		
$\Delta \log k$	± 0.3	298
$\Delta E/R$	± 500 K	
$\Delta k_1/k$	+0.0, -0.1	290-420

Comments on Preferred Values

The rate coefficients derived from the observed decay of t-C$_4$H$_9$O$_2$, k_{obs}, are in good agreement in all the reported studies, and provide a consistent description of the temperature dependence of the reaction. All the studies recognised the potential for secondary removal of t-C$_4$H$_9$O$_2$, resulting from the formation of CH$_3$O$_2$ and HO$_2$ from the chemistry following t-C$_4$H$_9$O decomposition, with each of these peroxy radicals reacting partially with t-C$_4$H$_9$O$_2$. This was taken into explicit account in the later analysis of Lightfoot et al. (1990) through simulation of the system, informed by the results of a number of product studies of the oxidation of t-C$_4$H$_9$ radicals (Thomas and Calvert, 1962; Kirsch and Parkes, 1981; Osbourne and Waddington, 1984). The preferred values of k are therefore based on the results of Lightfoot et al. (1990), but are clearly also consistent with the results of the other kinetics studies (Parkes, 1975; Anastasi et al., 1978). As discussed by Lightfoot et al. (1990), the derived value of k is sensitive to uncertainties in some of the parameters in the chemical mechanism (e.g., the branching ratios adopted for the CH$_3$O$_2$ + t-C$_4$H$_9$O$_2$ reaction: see datasheet ROO_43). The reliability of the preferred values reflects the reported level of sensitivity.

Although Kirsch and Parkes (1981) reported evidence for a minor product channel forming di-t-butyl peroxide and O$_2$ (k_2/k = 0.12 at 298 K, decreasing to zero at 373 K), neither of the other product studies (Thomas and Calvert, 1962; Osbourne and Waddington, 1984) found evidence for di-t-butyl peroxide formation. All these studies therefore support the operation of channel (1) as the dominant or exclusive product channel.

References

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