IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_2

This datasheet last evaluated: June 2018; last change in preferred values: June 2018.

$$C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2 \qquad (1)$$
$$C_2H_5O_2 + NO + M \rightarrow C_2H_5ONO_2 + M \qquad (2)$$
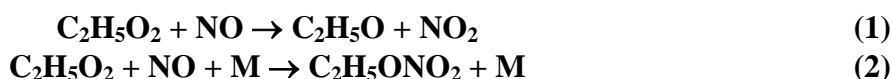
$\Delta H°(1) = -45.2 \text{ kJ·mol}^{-1}$

$\Delta H°(2) = -217.0 \text{ kJ·mol}^{-1}$

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

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/ Comments
Absolute Rate Coefficients			
$(2.7 \pm 0.2) \times 10^{-12}$	298	Adachi and Basco, 1979	FP-AS
$(8.9 \pm 3.0) \times 10^{-12}$	295	Plumb et al., 1982	DF-MS
$(8.5 \pm 1.2) \times 10^{-12}$	298	Sehested et al., 1993	PR-AS
$(8.2 \pm 1.6) \times 10^{-12}$	295	Däele et al., 1995	DF-MS (a)
$2.6 \times 10^{-12} \exp[(380 \pm 70)/T]$	207-403	Eberhard and Howard, 1996	F-CIMS (b)
$(9.3 \pm 1.6) \times 10^{-12}$	298		
$3.1 \times 10^{-12} \exp[(330 \pm 110)/T]$	220-355	Maricq and Szente, 1996	PLP-AS (c)
$(10.0 \pm 1.5) \times 10^{-12}$	295		
$3.8 \times 10^{-12} \exp[(290 \pm 110)/T]$	213-299	Ranschaert et al., 2000	F-CIMS (d)
$(10.1 \pm 0.9) \times 10^{-12}$	299		
$(11 \pm 0.8) \times 10^{-12}$	298	Xing et al., 2004	LP-MS (e)
$1.75 \times 10^{-12} \exp[(462 \pm 19)/T]$	203-298	Bardwell et al., 2005	F-CIMS (f)
$(8.03 \pm 0.35) \times 10^{-12}$	298		
Branching Ratio			
$k_2/k \leq 0.014$ (1 bar)	299	Atkinson et al., 1982	(g)
$k_2/k = 1.2 \times 10^{-3} \exp(610/T)$	213-298	Ranschaert et al., 2000	(h)
$k_2/k = 6 \times 10^{-3}$ (100 Torr N$_2$)	298		
$k_2/k = 20 \times 10^{-3}$ (100 Torr N$_2$)	213		
$k_1/k = 1.0 \pm 0.05$ (133-266 mbar N$_2$)	203-298	Bardwell et al., 2005	F-CIMS (f)
$k_2/k_1 = (7.4 \pm 1) \times 10^{-3}$ (100 Torr N$_2$)	298	Butkovskaya et al., 2010	F-CIMS (i)
$k_2/k_1 = (26.8 \pm 3.4) \times 10^{-3}$ (600 Torr N$_2$)			
$k_2/k_1 = 72.2 \times 10^{-3}$ (600 Torr N$_2$)	223		

Comments

(a) Conventional discharge flow system with LIF detection of C_2H_5O product. k determined by simulation of experimental C_2H_5O profiles.

(b) Ethylperoxy radicals formed by the thermal decomposition of n-propyl nitrate in the presence of O_2, or by RF discharge through C_2H_5I (also in the presence of O_2). Pseudo first order kinetics with excess NO and CIMS detection of $C_2H_5O_2$ as the ethyl peroxy negative ion.

(c) Excimer laser photolysis of Cl_2-C_2H_6-NO-O_2-N_2 mixtures. Time-resolved measurements of $C_2H_5O_2$ decay and C_2H_5ONO formation using diode array UV absorption spectroscopy, and of NO loss and NO_2 formation using diode laser absorption spectroscopy.

(d) Turbulent flow reactor at 100 Torr (133 mbar) N_2 total pressure. $C_2H_5O_2$ detected as $C_2H_5OOH^+(H_2O)_n$ and $C_2H_5ONO_2$ detected as $C_2H_5ONO_2H^+(H_2O)_n$ following proton transfer from H_3O^+.

(e) $C_2H_5O_2$ generated by reaction of C_2H_5 with O_2, whereby C_2H_5 radicals were generated in the 248 nm photolysis of C_2H_5I, the 193 nm photolysis of C_2H_5Br or the 193 nm photolysis of CCl_4 in the presence of ethane. Owing to poor sensitivity, the experiments could not be performed under pseudo first-order conditions, and the data obtained using CCl_4 are reported to be less reliable as a result of secondary chemistry. $C_2H_5O_2$ was detected as the negative parent ion following electron transfer from high Rydberg state rare gas atoms. The bath gas was 5.3 mbar He and 0.8 mbar O_2.

(f) Turbulent flow reactor at 133 or 266 mbar N_2 total pressure. $C_2H_5O_2$ was generated in the reaction $Cl + C_2H_6$ $(+O_2)$ and detected as $C_2H_5O_2^-$ following electron transfer from SF_6^-. Yield of NO_2 (detected as NO_2^-) was found to be 1.0 ± 0.05.

(g) GC analysis of $C_2H_5ONO_2$ product from photo-oxidation of C_2H_6 in Cl_2-C_2H_6-NO-air mixtures.

(h) Temperature dependent values of the rate coefficient $k_2 = 1.6 \times 10^{-15}$ exp $(1160/T)$ for the temperature range 213 to 299 K and 100 Torr (133 mbar) N_2 pressure also presented. The authors state that the branching ratios are associated with large errors as the measurements were conducted near the detection limit for $C_2H_5ONO_2$ and were complicated by secondary chemistry.

(i) Turbulent flow reactor with CIMS detection of products. Branching ratios (k_2 / k_1) were derived from monitoring the formation of $C_2H_5ONO_2$ relative to either NO_2, C_2H_5ONO or CH_3CHO, the latter two both arising from reactions of alkoxy radical co-product of NO_2 in reaction (1). The in-situ calibration of $C_2H_5ONO_2$ and C_2H_5ONO was via formation of C_2H_5O at known yield (0.55) in the reaction of F atoms with C_2H_5OH and its further reactions with NO_2 or NO, respectively. Consistent results were reported when using NO_2, C_2H_5ONO or CH_3CHO as a measure of the flux through reaction (1).

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	9.1×10^{-12}	298
k /cm^3 molecule^{-1} s^{-1}	2.55×10^{-12} exp$(380/T)$	200-410
k_2/k *	$(1/(0.01 \times (1.18e\text{-}19 \times[M]+0.365) \times (1+900 \times (1/T\text{-}1/298)))+1)^{-1}$	
k_2/k (1 bar)	0.033	298 K
Reliability		
$\Delta \log k$	± 0.1	298
$\Delta E/R$	± 50	200-410

$\Delta \log (k_2/k)$	± 0.2		220-320

*The expression was adapted from the parameterization for k_2/k_1 given by Butkovskaya et al. (2010) using $k_2/k = (k_1/k_2 +1)^{-1}$.

Preferred Values

Comments on Preferred Values

With the exception of the measurement of Adachi and Basco (1979), all measurements at room temperature are in reasonable agreement. The preferred value of the rate coefficient at room temperature is an average of the data from the direct studies of Plumb et al. (1982), Eberhard and Howard (1996), Ranschaert et al. (2000) and Bardwell et al. (2005). The temperature coefficients (*E/R*) also show good agreement and the preferred value was obtained from a weighted fit to the data of Eberhard and Howard (1996), Ranschaert et al. (2000) and Bardwell et al. (2005). The data of Maricq and Szente (1996) are consistent with these datasets, but significantly more scattered.

The observation of a temperature independent, $(100 \pm 5)\%$ yield of NO_2 confirms that the reaction proceeds predominantly via formation of an alkoxy radical + NO_2 under atmospheric conditions (Bardwell et al., 2005), with low yields of $C_2H_5ONO_2$ at room temperature (Atkinson et al., 1982). However, the work of Ranschaert et al. (2000) and Butkovskaya et al, (2010) indicate that the yield of $C_2H_5ONO_2$ increases with increasing pressure and decreasing temperature. The extensive experiments of Butkovskaya et al. (2010), covering temperatures between 222 and 323 K and pressures between 100 and 600 Torr, enabled the authors to derive a pressure and temperature dependent expression for k_2/k_1, which reproduces their own data and is roughly consistent with the observations of Raenschaert et al (2000). The data of Butkovykaya et al (2010) are reasonably consistent with predictions of temperature dependent nitrate formation in $C_2H_5O_2$ + NO extrapolated from larger RO_2 (Carter and Atkinson, 1985) but not with latter recommendations from the same group (Carter and Atkinson, 1989, Arey et al., 2001).

We have adopted the parameterisation of Butkovykaya et al (2010) as our preferred branching ratio for ethyl-nitrate formation, but have expanded the uncertainty to account for the difference between their results at one bar and room temperature compared to Atkinson et al. (1982).

References

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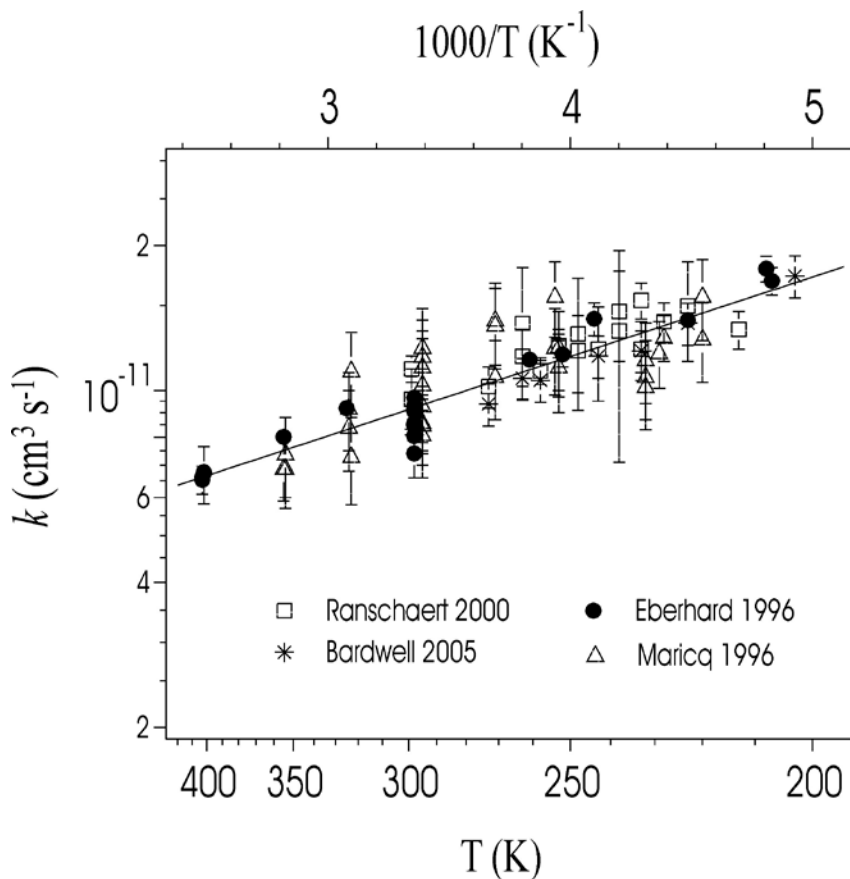
Rate coefficients (k) for $C_2H_5O_2$ + NO. The solid line is the IUPAC preferred value.
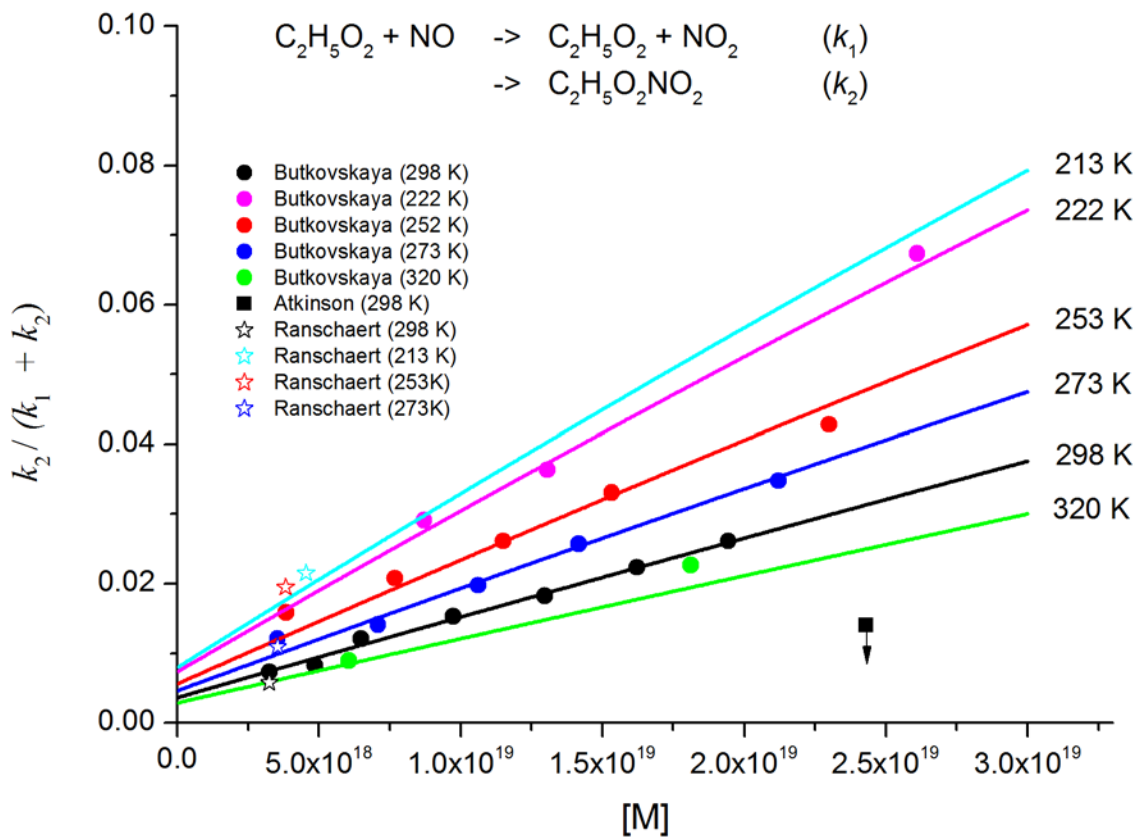
Branching ratio, $k_2 / (k_1+k_2)$, for formation of $C_2H_5ONO_2$ in the reaction between $C_2H_5O_2$ and NO. The solid lines are adapted from the parameterisation given by Butkovykaya et al. (2010). To preserve clarify of presentation, only selections of the datasets of Butkovskaya et al. (2010) and Ranschaert et al. (2000) are shown. The down-arrow on the data point of Atkinson (1982) indicates an upper-limit.