IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet CGI_20

This datasheet first evaluated: March 2017; last change in preferred values: March 2017.

$(CH_3)_2COO + NO_2 \rightarrow (CH_3)_2COO + NO_3$ (1)
$(+ M) \rightarrow (CH_3)_2COONO_3$ (2)

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

k/cm^3 molecule^{-1} s^{-1}	Temp /K	Reference	Technique/Comments
Absolute Rate Coefficients			
$(2.3 \pm 2.5) \times 10^{-12}$	293	Chhantyal-Pun,et al., 2017	PLP-PIMS(a)
$(2.1 \pm 0.3) \times 10^{-12}$ (for $(CD_3)_2COO$)	293		

Comments

(a) $(CH_3)_2COO$ (acetone oxide) was ~~produced by the reaction of $(CH_3)_2CI + O_2$. CH_3CHI was~~ generated by 248-nm laser photolysis of 2,2-diiodopropane, $(CH_3)_2CI_2$, at 293 K and 4 Torr, in a large excess of O_2. ~~The reacting mixture was monitored by t~~Tunable synchrotron PIMS ~~at m/z = 74 which~~ was used to measure time-dependence of $[(CH_3)_2COO]$ in the gas phase. ~~The kinetics of decay was used to determine the rate constants.~~ A ~~However~~ large background signal ~~a persistent background~~ at m/z = 74 prevented reliable measurement of the rate coefficient. ~~for the reaction of $(CH_3)_2COO$ with NO_2 from the slope of the first order decay plots of $(CH_3)_2COO$ in the presence of excess known concentrations of NO_2. The derived k values had a 95% uncertainty bound larger than the value of the second-order rate coefficient itself.~~ The ~~The~~ cited result, $(2.3 \pm 2.5) \times 10^{-12}$ cm^3 s^{-1}, should therefore be interpreted as an upper limit value of the rate coefficient of $k((CH_3)_2COO + NO_2) \leq 5 \times 10^{-12}$ cm^3 s^{-1}. However, in the case of $(CD_3)_2COO$ the background had a negligible effect, allowing accurate measurement of its rate coefficient for reaction with NO_2.

Preferred Values

Parameter	Value	T/K
k/cm^3 molecule^{-1} s^{-1}	2.1×10^{-12}	293
Reliability		
$\Delta \log k$	0.3	293

Comments on Preferred Values

The reported measurements on the overall reaction of $(CH_3)_2COO$ with NO_2 suffer from interference from a background but the rate coefficient for the deuterated form, $(CD_3)_2COO$, is similar to that for both *syn*- and *anti*-CH_3CHOO reacting with NO_2: $k(CH_3CHOO + NO_2) = (2 \pm 1) \times 10^{-12}$ cm^3 s^{-1} reported by Taatjes et al.(2013), which is the basis of the IUPAC recommendation for overall $k(CH_3CHOO + NO_2) = (2 \pm 1) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, for both conformers (data sheet: CGI_17). A rate coefficient of similar magnitude for the reaction of CH_2COO with NO_2 was obtained by Stone et al.(2014), who measured a k value of $(1.5 \pm 0.5) \times 10^{-12}$ cm^3 s^{-1}, independent of pressure in the range 25 – 300 Torr. (data sheet: CGI_17). The earlier value of reported by Weltz et al. (2012), who also used PIMS to measure $k(CH_2COO + NO_2)$ was higher but had a larger experimental uncertainty. The overall body of data appears to show that all carbonyl oxides react with NO_2 with similar rates

The products of the reactions of Criegee intermediates with NO_2 are usually presumed to be NO_3 and a carbonyl compound (in this case acetone). Attempts to measure NO_3 products from the reaction of $(CD_3)_2COO$ with NO_2 failed, as have similar attempts for other carbonyl oxide reactions with NO_2. However there are several possible association channels leading to an addition complex, and ~~eventual~~ nitrate production observed in ozonolysis experiments may result from further reaction of this complex.

References

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