IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_20

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

$(CH_3)_2COO + NO_2 \rightarrow$ products

Rate coefficient data

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 (c)
$(2.1 \pm 0.3) \times 10^{-12}$ ($(CD_3)_2COO$)	293		

Comments

(a) $(CH_3)_2COO$ was generated by 248 nm laser photolysis of $(CH_3)_2CI_2$ at 293 K and 4 Torr, in a large excess of O_2. Tunable synchrotron PIMS was used to measure time-dependence of [$(CH_3)_2COO$] in the gas phase. A large background signal at m/z = 74 prevented reliable measurement of the rate coefficient. The cited result, $(2.3 \pm 2.5) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, should therefore be interpreted as an upper limit value of $k \leq 5 \times 10^{-12}$ cm^3 molecule^{-1} 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, as tabulated above.

Preferred Values

Parameter	Value	T/K
k/ cm^3 molecule^{-1} s^{-1}	2.1×10^{-12}	298
Reliability		
$\Delta \log k$	± 0.3	298

Comments on Preferred Values

The reported measurement of k for the reaction of $(CH_3)_2COO$ with NO_2 suffers from interference from a background signal. However, that for the deuterated form, $(CD_3)_2COO$, is similar to those for CH_2OO and both *Z*- and *E*-CH_3CHOO reacting with NO_2 (see data sheets CGI_2 and CGI_17). The overall body of data therefore appears to show that all Criegee intermediates react with NO_2 with similar rates, with k close to 2×10^{-12} cm^3 molecule^{-1} s^{-1}.

Attempts to measure NO_3 from the reaction of $(CD_3)_2COO$ with NO_2 failed (Chhantyal-Pun et al., 2017), as have similar attempts for other sCI reactions with NO_2 (Taatjes et al., 2013; Caravan et al., 2017). However, there are several possible association channels leading to addition complexes, and nitrate production observed in ozonolysis experiments may result from further reaction of these complexes. Caravan et al (2017) have shown conclusively that a stable addition product accounts for the major fraction of the products of the reaction of *Z*-CH_3CHOO with NO_2.

References

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