

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_3

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CH₂OO + NO → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$< 6 \times 10^{-14}$	298	Welz et al., 2012	PLP-PIMS (a)
$< 2 \times 10^{-13}$	295	Stone et al., 2014	PLP-LIF/PIMS (b)

Comments

- (a) CH₂OO was produced by the reaction of CH₂I + O₂. CH₂I was generated by 248 nm laser photolysis of di-iodomethane, CH₂I₂, at 298 K and 4 Torr total pressure in a large excess of O₂. The reacting mixture was monitored by tunable synchrotron photo-ionization mass spectrometry, which allowed characterisation of the PIMS for CH₂OO and its reaction products over the region 9.5 – 11.5 eV. Time-resolved direct detection of CH₂OO at $m/z = 46$ amu. The first order decay CH₂OO in the presence of 5×10^{15} molecule cm⁻³ NO was unaffected leading to the cited upper limit for k , based on the assumption that a 25% increase on the decay constant could be detected.
- (b) Laser photolysis at 248 nm of CH₂I₂-O₂-N₂ mixtures was used to produce CH₂OO in the presence of excess NO ($0.36 - 1.7 \times 10^{15}$ molec.cm⁻³). Kinetics of CH₂OO followed by time-resolved monitoring of HCHO reaction products by laser-induced fluorescence (LIF), which exhibited exponential growth (1st order kinetics) on two timescales. The fast HCHO production is assigned to the reaction of CH₂IO₂ with NO and the slower growth due to CH₂OO reactions. The upper limit for k was based on the observation of no effect of [NO] on the slow growth curves, assuming the HCHO production was due to the reaction with NO.

Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$< 6 \times 10^{-14}$	298

Comments on Preferred Values

The only studies of the reaction kinetics are those of Welz et al. (2012) and of Stone et al. (2014), who both reported upper limits for k . These results are consistent but the preferred upper limit is the lower value from Welz et al. (2012), as their monitoring of [CH₂OO] is more direct and the possible interferences are less. Since no clear reaction has been observed, the products under atmospheric conditions are not known. Theoretical calculations (Vereecken et al., 2012) using DFT methods found

the CH₂OO + NO reaction to show a barrier at all levels of theory employed. The lowest entrance transition state was found for the formation of a cyclic adduct with a nitrogen-centered radical, with a barrier calculated at 5.8 kcal mol⁻¹. The estimated rate coefficient, 1.7×10^{-18} cm³ molecule⁻¹ s⁻¹, is well below the experimental value of Welz et al. (2012).

References

- Stone, D., Blitz, M., Daubney, L., Howes, N. U. M. and Seakins, P.: Phys. Chem. Chem. Phys., 16, 1139, 2014.
- Vereecken, L., Harder, H. and Novelli, A.: Phys. Chem. Chem. Phys., 14, 14682, 2012.
- Welz, O., Savee, J. D., Osborn, D. L., Vasu, S. S., Percival, C. J., Shallcross, D. E. and Taatjes, C. A.: Science, 335, 204, 2012.