

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI_17

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This datasheet last evaluated: February 2019; last change in preferred values: February 2019

CH₃CHOO (*Z*- and *E*-) + NO₂ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2 \pm 1) \times 10^{-12}$	298	Taatjes et al., 2013	PLP-PIMS (a)
$k_{(Z)} = (2.0 \pm 0.3) \times 10^{-12}$	298		
$k_{(E)} = (3.1 \pm 1.1) \times 10^{-12}$	298		
$k_{(Z)} = (1.7 \pm 0.3) \times 10^{-12}$ (20 Torr)	300	Caravan et al., 2017	PLP-PIMS (b)
$k_{(Z)} = (2.0 \pm 0.3) \times 10^{-12}$ (40 Torr)	300		

Comments

- (a) CH₃CHOO was produced by the reaction of CH₃CHI + O₂. CH₃CHI was generated by 248 nm laser photolysis of 1,1-diiodoethane, CH₃CH₂I₂, at 298 K and 4 Torr, in a large excess of O₂. The reacting mixture was monitored by tunable synchrotron photoionization mass spectrometry, which allowed characterisation of the PIMS. Both *Z*- and *E*-CH₃CHOO are produced, which could be distinguished by the difference in the ionisation energy of the two conformers. The first order decay plots of *Z*- and *E*-CH₃CHOO in the presence of excess known concentrations of NO₂ were used to determine the rate constants. The cited values were given by unweighted fits of the data, with uncertainty limits of 95%; returns from weighted fits gave k values lower by 30% but also indicated a slightly larger value for *E*- conformer. Although a small (statistically significant at 1 σ level) conformer dependence was reported, their preferred recommendation is $k = (2 \pm 1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, for both conformers.
- (b) CH₃CHOO was produced by the reaction of CH₃CHI + O₂. CH₃CHI was generated by 248-nm pulsed laser photolysis of 1,1-diiodoethane, CH₃CH₂I₂, at 300 K and pressures of 20 and 40 Torr, in a large excess of O₂. The reacting mixture was monitored by PIMS at 10.5 eV, which allowed kinetic decay attributed to the *Z*- conformer of CH₃CHOO to be monitored. The first order decay plots in the presence of excess NO₂ (0 – 6.5 molecule cm⁻³) were used to determine the rate constants. Products were investigated using multiplexed photoionization mass spectrometry.

Preferred Values

Parameter	Value	T/K
$k_{(Z-)} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.0×10^{-12}	298
$k_{(E-)} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	2.0×10^{-12}	298
<i>Reliability</i>		
$\Delta \log k_{(Z-)}$	± 0.15	298
$\Delta \log k_{(E-)}$	± 0.3	298

Comments on Preferred Values

The reported measurements on the overall rate coefficient for the reaction of *Z*- and *E*-CH₃CHOO with NO₂ from the two studies show good agreement. In the study of Taatjes et al. (2013) a slightly faster reaction with the *E*- conformer (statistically significant at 1 σ confidence interval) was reported. However, the experiments suffered from low signal quality, and the conformer dependence was not well defined. The Caravan et al. (2017) kinetic measurements were confined predominantly to the *Z*-conformer of CH₃CHOO, and reported a barely significant pressure dependence over the range 20–40 Torr.

Earlier efforts to characterize the yield of NO₃ from this and other sCI + NO₂ reactions have been inconclusive. Many studies have failed to detect NO₃, including Caravan et al. (2017) over a pressure range of 4–40 Torr. However, a temporally resolved and [NO₂]-dependent signal was observed at the mass of the Criegee-NO₂ adduct for both the CH₂OO and CH₃CHOO systems, and the structure of this adduct was explored through *ab initio* calculations. Its origin from a direct CI reaction was demonstrated by observation of its efficient scavenging by SO₂. It is postulated that this adduct is the major reaction product and, based on the acetaldehyde signal, an upper limit of < 30 % is placed on the NO₃ + acetaldehyde yield. The fate of these Criegee-NO₂ adducts requires further investigation to fully understand the impact of this reaction on tropospheric NO_x.

References

- Caravan, R. L., Khan, M. A. H., Rotavera, B., Papajak, E., Antonov, I. O., Chen, M.-W., Au, K., Chao, W., Osborn, D. L., Lin, J. J.-M., Percival, C. J., Shallcross, D. E., and C. A. Taatjes: Faraday Discuss., 200, 313, 2017.
- Taatjes, C. A., Welz, O.; Eskola, A. J., Savee, J. D., Scheer, A. M., Shallcross, D. E., Rotavera, B., Lee, E. P. F., Dyke, J. M., Mok, D. K. W., Osborn, D. L., and Percival, C. J.: Science, 340, 171, 2013.