**IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet CGI\_20**

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

**(CH3)2COO + NO2 → products**

## Rate coefficient data

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *k*/cm3 molecule-1 s-1 | Temp./K | Reference | | Technique/Comments |
| *Absolute Rate Coefficients* |  | |  |  |
| (2.3 ± 2.5) × 10-12 | 293 | Chhantyal-Pun et al., 2017 | | PLP-PIMS (c) |
| (2.1 ± 0.3) × 10-12 ((CD3)2COO) | 293 |  | |  |

##### Comments

1. (CH3)2COO was generated by 248 nm laser photolysis of (CH3)2CI2 at 293 K and 4 Torr, in a large excess of O2. Tunable synchrotron PIMS was used to measure time-dependence of [(CH3)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 ± 2.5) × 10−12 cm3 molecule-1 s-1, should therefore be interpreted as an upper limit value of *k* ≤ 5 × 10−12 cm3 molecule-1 s-1. However, in the case of (CD3)2COO the background had a negligible effect, allowing accurate measurement of its rate coefficient for reaction with NO2, as tabulated above.

##### Preferred Values

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | **T/K** |
|  |  |  |
| *k*/ cm3 molecule-1 s-1 | 2.1 × 10-12 | 298 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  log *k* | ± 0.3 | 298 |

1. *Comments on Preferred Values*
2. The reported measurement of *k* for the reaction of (CH3)2COOwith NO2 suffers from interference from a background signal. However, that for the deuterated form, (CD3)2COO, is similar to those for CH2OO and both *Z-* and *E-*CH3CHOO reacting with NO2 (see data sheets CGI\_2 and CGI\_17). The overall body of data therefore appears to show that all Criegee intermediates react with NO2 with similar rates, with *k* close to 2 × 10-12 cm3 molecule-1 s-1.
3. Attempts to measure NO3 from the reaction of (CD3)2COO with NO2 failed (Chhantyal-Pun et al., 2017), as have similar attempts for other sCI reactions with NO2 (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*-CH3CHOO with NO2.

**References**

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