IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet Het\_Org3

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 **NO3 + saturated alcohols / carbonyls**

**Experimental data**

|  |  |  |  |
| --- | --- | --- | --- |
| *Parameter*  | Temp./K | Reference | Technique/ Comments |
| γ0  |  |  |  |
| (2.1 ± 0.3) × 10-3 (n-octanoic acid) | 290 | Moise et al., 2002 | CWFT-AS (a) |
| (7.1 ± 1.6) × 10-3 (1-octanol) | 258 |  |  |
| (0.8 – 1.7) × 10-3 (glycerol) | 268-293 | Gross et al., 2009 | CWFT-CIMS (b) |
| (3.5 - 4.5) × 10-3 (diethyl sebacate) | 278-298 |  |  |
| (4.4 ± 0.4) × 10-3 (diethyl sebacate) | 278 | Xiao and Bertram, 2011 | CWFT-CIMS (b) |
| (3.9 ± 0.3) × 10-3 (dioctyl sebacate) | 278 |  |  |
| (16 ± 8) × 10-3 (tridecanal) | 263 | Iannone et al., 2011 | CWFT-CIMS (c)  |
| 0-12 × 10-3 (tridecanal in organic matrix) | 275 |  |  |
| (1-3) × 10-3 (levoglucosan) | 298 | Knopf et al., 2011 | CWFT-CIMS (d) |
| (6 ± 1) × 10-3 (16-mercapto-1-hexadecanol, SAM) | RT | Zhang and Morris, 2015 | RAIRS (e) |
|  |  |  |  |

diethyl sebacate is C2H5OC(O)(CH2)8C(O)OC2H5), dioctyl sebacate is (CH2)8(C(O)OC8H17)2), Levoglucosan (C6H10O5) is (1*R*,2*S*,3*S*,4*R*,5*R*)-6,8-Dioxabicyclo[3.2.1]octane-2,3,4-triol. RT = room temperature.

Comments

1. Rotating, coated wall flow tube. NO3 (5-50 × 1011 molecule cm‑3) was formed by the thermal dissociation of N2O5 and detected by diode laser absorption at 662 nm.
2. Rotating, coated wall flow tube. NO3 (3.5-16 × 1010 molecule cm‑3) was formed by the thermal dissociation of N2O5 and detected following ionisation by I-. The uptake coefficient for diethyl sebacate decreased by a factor ~10 upon freezing.
3. NO3 (3.6-8.5 × 1011 molecule cm‑3) was formed by the thermal dissociation of N2O5 and detected following ionisation by I-. Tridecanal was solid at 263 K or was dissolved in diethyl sebacate, dioctyl sebacate or squalane for experiments at 275 K.
4. NO3 (4-300 × 109 molecule cm‑3) was formed by the thermal dissociation of N2O5 and detected following ionisation by I-. The higher values of γ were obtain at lowest NO3 concentrations. Levoglucosan was solid at the experimental temperature.
5. γ derived by observing loss rate of terminal hydroxyl groups and calculating surface-near NO3 concentratons.

**Preferred Values**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | **T/K** |
| *α*b | 1 |  |
| *k*b (M-1 s-1) | 6 × 104 | 270-300 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  |  |  |
| Δ log(*k*b) | 0.6 |  |
|  |  |  |

Comments on Preferred Values

Uptake to liquid saturated alcohols and carbonyls is relatively slow with uptake coefficients between 10-3 and 10-2. The highest values are obtained with organics that also are expected to have more rapid gas-phase reactions with NO3 (e.g. aldehydes).

The uptake coefficients for n-octanoic acid, 1-octanol and diethyl sebacate decreased significantly when the surface was frozen at lower temperatures, which was attributed to the reduced rate of diffusion of NO3 into the bulk sample (Moise et al., 2002; Gross et al., 2009). In addition, γ for glycerol is lower than expected given trends in gas-phase reactivity and this is also attributed to its high viscosity limiting diffusion through the bulk sample (Gross et al., 2009). Iannone et al (2011) showed that the uptake coefficient for NO3 reacting with tridecanal depended on its concentration and on the matrix organic with values of $H\sqrt{k\_{bi}D\_{l}}$ of 9.4, 6.9 and 3.6 cm M0.5 atm-1 s-1 for NO3 uptake and reaction with tridecanal in DES, DOS and squalane, respectively.

Thus, if the reaction between NO3 and the saturated alcohol / carbonyl (of concentration [HC], in units of mol L-1) takes place throughout the particle, the uptake coefficient can be described by

$$γ=\left\{\frac{1}{α\_{b}}+\frac{\overbar{c}}{4HRT\sqrt{Σ(k\_{b(i)}[HC]\_{(i)})D\_{l}}}\right\}^{-1}$$

Where *k*b(i) is the liquid-phase rate coefficient for reaction of NO3 with organic species (i)with concentration [HC], *Dl* its diffusion coefficient through the organic matrix and *H* its solubility.

A rough estimate for a generic uptake coefficient for NO3 uptake to saturated alcohols or carbonyls can be made using *kb*= 6 × 104 M-1 s-1 (equivalent to a gas-phase rate constant of 1 × 10-16 cm3 molecule-1 s‑1), *Dl*, = 2 × 10-5 cm2 s-1, and *H* = 0.8 Matm-1, this expression results in a value of γ = 5 × 10-3, which is consistent with the experimental data if we assign an uncertainty of a factor 4. The large uncertainty associated with use of a generic rate constant, *k*b, and also use of potentially inappropriate values of *H* and *Dl*  is taken into account by assigning a large uncertainty to *kb*.

Uptake to multicomponent organic mixtures can be approximated by summing the product *k*b(i)[HC](i) and using an average value for *H* and *Dl*. For unreactive or very small particles a correction for the diffuso-reactive length may be important (see guide to datasheets), whereas for very reactive particles, the reaction my be limited to the surface layers of the sample. This may result in uptake coefficients that decrease with exposure time if mixing in the particle is hindered by high viscosity. The NO3 concentration- and time-dependence of the uptake coefficient to a sample of levoglucosan could be described with a multilayer model of surface and bulk reactions and bulk diffusion of NO3 (Shiraiwa et al., 2012).

The reaction of NO3 with the saturated organics considered here proceeds largely through abstraction. Zhang and Morris (2015) observed formation of organic nitrates simultaneously with loss of terminal CH2OH groups and concluded that reaction proceeds via abstraction at terminal –CH2OH group.

References

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