IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet Het\_Org1

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This data sheet evaluated: June 2016; last change in preferred values: June 2016.

**NO3 + alkanes**

**Experimental data**

|  |  |  |  |
| --- | --- | --- | --- |
| *Parameter* | Temp./K | Reference | Technique/ Comments |
| γ0 |  |  |  |
| (2.6 ± 0.8) × 10-3 (n-hexadecane) | 293 | Moise et al., 2002 | CWFT-AS (a) |
| (14 ± 2) × 10-3 (n-hexadecane, SAM) | 293 | Knopf et al. 2006 | CWFT-CIMS (b) |
| (8.8 ± 2.5) × 10-4 (octadecanethiol, SAM) | 298 |  |  |
| (5.2 ± 0.4) × 10-3 (squalane) | 278 | Xiao and Bertram, 2011 | CWFT- CIMS (c) |
| < 7.8 × 10-3 (squalane) | 293 | Lee et al., 2013 | AFT –AMS (d) |
| (2.1 ± 0.8) × 10-3 (heptamethylnonane) | 253 | Moise et al., 2002 | CWFT-AS (a) |
|  |  |  |  |

Squalane is C30H62 (2,6,10,15,19,23-Hexamethyltetracosane). SAM = self-assembled monolayer.

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. Coated wall flow tube with n-hexadecane or octadecanethiol present as self-assembeld monolayers. NO3 (2-4 × 1011 molecule cm‑3) was formed by the thermal dissociation of N2O5 and detected following ionisation by I-.
3. NO3 (3-16 × 1010 molecule cm‑3) was formed by the thermal dissociation of N2O5 and detected following ionisation by I-.
4. ~ 100 nm particles of squalane. Measurements performed using a mixture of NO3 and N2O5, with N2O5 monitored as NO2 following thermal dissociation. The uptake coefficient for NO3 reacting with the squalane was calculated assuming no heterogeneous loss of N2O5 and is thus an upper limit.

**Preferred Values**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | **T/K** |
| *α*b | 1 |  |
| *k*b (M-1 s-1) | 6 × 104 | 280 - 300 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  |  |  |
| Δ log(*k*b) | 0.7 |  |
|  |  |  |

Comments on Preferred Values

Uptake to liquid saturated hydrocarbons is relatively slow with initial uptake coefficients between 10-3 and 10-2. Moise et al ([Moise et al., 2002](#_ENREF_29)) found that (for a solid sample) uptake to a branched chain alkane was more efficient than for a branched alkane, which is consistent with known trends in gas-phase reactivity of NO3. The uptake coefficient 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.

If the reaction between NO3 and the alkane (of concentration [HC], in units of mol L-1) takes place throughout the particle, the uptake coefficient can be described by

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

A rough estimate for a generic uptake coefficient for NO3 uptake to an alkane can be made using *k*b = 6 × 104 M-1 s-1 which is 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 results in a value of γ = 5 × 10-3, which is consistent with the experimental data within the uncertainty assigned to *k*b. 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.

In their experiments on octadecanethiol, Knopf et al. (2006) observed formation of condensed phase carbonyl species and no evidence for significant volatilisation of the organic substrate. In further experiments, the same group (Gross and Bertram, 2009) observed formation of organonitrate products for the same alkane. In contrast, gas-phase product analysis in the experiments of Lee et al. (2013) on squalene showed that NO3 was converted stoichiometrically to NO2.

References

Gross, S. and Bertram, A. K.: J. Geophys. Res. 114, D02307, doi: 10.1029/2008JD010987, 2009.

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Moise, T., Talukdar, R. K., Frost, G. J., Fox, R. W. and Rudich, Y.: J. Geophys. Res.-Atmos. 107, D2, doi: 10.1029/2001JD000334,2002.

Xiao, S., and Bertram, A.K.: Phys. Chem. Chem. Phys. 13, 6628-6636, 2011.