IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet Het\_Org2

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

 **NO3 + alkenes**

**Experimental data**

|  |  |  |  |
| --- | --- | --- | --- |
| *Parameter*  | Temp./K | Reference | Technique/ Comments |
| γ0  |  |  |  |
| (1.6 ± 0.3) × 10-3 (1-octadecene) | 293  | Moise et al., 2002 | CWFT-AS (a) |
| (2.3 ± 0.9) × 10-3 (1-hexadecene) | 277  |  |  |
| (5.8 ± 2.0) × 10-3 (7-tetradecene) | 246  |  |  |
| $(34\_{-18}^{+ 44}$) × 10-3 (undec-10-ene-1-thiol, SAM) | 298  | Gross and Bertram, 2009 | CWFT-CIMS (b) |
| ($140\_{-50}^{+ 860}$) × 10-3 (methyl oleate) | 278 | Xiao and Bertram, 2011 | CWFT-CIMS (c) |
| (180 ± 30) × 10-3 (squalene) | 293 | Lee et al., 2013 | AFT-AMS (d) |
| (2.3 ± 0.5) × 10-3 (17-octadecene-1-thiol, SAM) | RT | Zhang et al., 2014 | RAIRS (e) |
|  |  |  |  |

RT = room temperature, squalene is C30H62 (2,6,10,15,19,23-Hexamethyltetracosane),

methyl oleate is CH3(CH2)7CH=CH(CH2)7CO2CH3

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. NO3 (1-2 × 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-. The uptake coefficient decreased by a factor of 10 following surface exposure to NO3 for 90 mins.
4. ~ 100 nm particles of squalene. 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 squalene was calculated assuming no heterogeneous loss of N2O5.
5. γ derived by observing loss rate of terminal double bonds and calculating surface-near NO3 concentratons.

**Preferred Values**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | **T/K** |
| *α*b | 1 |  |
| *k*b (M-1 s-1) | 1.2 × 106 | 270 - 300 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  |  |  |
| Δ log(*k*b) | 1 |  |

Comments on Preferred Values

NO3 adds to double bonds and the experimentally derived uptake coefficient for NO3 reacting with alkenes varies by ~ two orders of magnitude, with the largest values obtained with squalene (six double bonds) (Lee et al., 2013). Lee et al. (2013) report that the uptake coefficient increased with exposure time (to 0.8 ± 0.1) indicating that the nitrated products are more reactive to NO3 than squalene itself. In contrast, both Gross and Bertram (2009) and Zhang et al. (2014) found that γ decreased with exposure as vinyl groups were consumed.

Gross and Bertram (2009) suggest that the larger γ0 values they get for undec-10-ene-1-thiol (a SAM with a terminal, single double-bond) compared to values reported by Moise et al. (2002) for liquid alkenes, with a single double-bond may be due to the location of the (reactive) double-bond at the gas-surface interface. The very high value of γ0 for methyl-oleate, may partially reflect the high electron density around the double bond of the branched alkene.

 Xiao and Bertram (2011) investigated the uptake of NO3 to methyl oleate in binary mixtures of less reactive, saturated organics such as squalane, diethyl sebacate (DES) and dioctyl sebacate (DOS). The results could be described by the usual resistor model:

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

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.

Xiao et al derived values of $H\sqrt{k\_{bi}D\_{l}}$ of 69.4, 35.4 and 26.1 cm M0.5 atm-1 s-1 for NO3 uptake and reaction with methyl oleate in DES, DOS and squalane, respectively. The lower values indicate that the diffusion term (*Dl*) influences the uptake coefficient significantly.

A rough estimate for a generic uptake coefficient for NO3 uptake to an alkene can be made by using *k*b = 1.2 × 106 M-1 s-1 which is equivalent to a gas-phase rate constant of 2 × 10-15 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 = 2 × 10-2, which is consistent with the experimental data if we assign a total uncertainty of a factor 10. 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.

Lee et al found that ~ 1.5 squalene molecules were reacted per NO3 taken up, indicating that secondary consumption of squalene was operative and that, under their conditions of concentration and exposure time up to three NO3 subunits added to the squalene backbone during reaction. The formation of consensed-phase organonitrates and carbonyls has also been documented (Gross et al., 2009; Zhang et al. (2014).

References

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