IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet Het\_Org5

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

**NO3 + aromatics**

**Experimental data**

|  |  |  |  |
| --- | --- | --- | --- |
| *Parameter* | Temp./K | Reference | Technique/ Comments |
| γ0 |  |  |  |
| > 0.1 (pyrene) | 293 | Mak et al., 2007 | CWFT-CIMS (a) |
| (pyrene) | 273 | Gross and Bertram, (2008) | CWFT-CIMS (b) |
| (pyrene) | 293 - 297 |  |  |
| (benz[a]anthracene) | 273 |  |  |
| (benz[a]anthracene) | 293 - 297 |  |  |
| (fluoranthene) | 273 |  |  |
| 0.02-0.03 (nitroguaiacol) | 298 | Knopf et al., (2011) | CWFT-CIMS (c) |
| 0.37 (pyrene) | 287 | Liu et al., (2012) | Chamber AMS/GC-MS (d) |
| 0.06 (1-nitro-pyrene) | 287 |  |  |
| 0.57 (1-hydroxy-pyrene) | 287 |  |  |
| 0.29 (benz[a]anthracene) | 287 |  |  |
| 0.18 (chrysene) | 287 |  |  |
|  |  |  |  |

Pyrene is C16H10 (benzo[def]phenanthrene), benz[a]anthracene is C18H12, Fluoranthene is C16H10, nitroguaiacol (C7H7NO4) is 2-methoxy-5-nitrophenol, chyrsene (C18H12) is 1,2-Benzophenanthrene.

Comments

1. NO3 (7-40 × 1010 molecule cm‑3) was formed by the thermal dissociation of N2O5 and detected following ionisation by I-. Pyrene surfaces were solid.
2. NO3 (3-37 × 1010 molecule cm‑3) was formed by the thermal dissociation of N2O5 and detected following ionisation by I-. Pyrene surfaces were solid. The initial values of γ listed decreased with exposure to NO3 for samples at 263 K. This effect was greatly reduced for benz[a]anthracene, and absent for pyrene and fluoranthene at 297 K.
3. NO3 (4-300 × 109 molecule cm‑3) was formed by the thermal dissociation of N2O5 and detected following ionisation by I-. The larger values of γ0 were obtained when using low NO3 concentrations.
4. NO3 present in equilibrium mixtures of NO2-NO3-N2O5. Aromatics present as coatings on an azelaic acid particle. Relative loss rate of aromatic (particle) and isoprene (g) monitored to derive γ. Correction for the diffusive limitation to the uptake was achieved by normalising to γ obtained by ([Gross and Bertram, 2008](#_ENREF_2)) and (Mak et al., 2007).

**Preferred Values**

|  |  |  |
| --- | --- | --- |
| **Parameter** | **Value** | **T/K** |
| *α*b | 1 |  |
| *k*b (M-1 s-1) | 3 × 108 | 280-300 |

*Reliability*

|  |  |  |
| --- | --- | --- |
|  |  |  |
| Δ log(*k*b) | 0.5 |  |
|  |  |  |

Comments on Preferred Values

Early work (Pitts et al., 1985) on NO3 / N2O5 interactions with pyrene assigned product formation to reaction with N2O5 and found no evidence for reaction with perylene. Subsequent research has shown that NO3 is taken up efficiently to several aromatics, with γ generally between 0.1 and 1.

If the reaction between NO3 and the unsaturated acid (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)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 aromatics can be made using *kb*= 3 × 108 M-1 s-1 (equivalent to a gas-phase rate constant of 5 × 10-13 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 = 0.3, 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 products formed by reacting NO3 with ambient, particulate phase aromatics are nitropyrenes, nitrofluoranthenes, anthracene, nitro-chrysene and nitrobenzo(a)pyrene (Zimmermann et al., 2013). Laboratory studies have identified the following products from reaction of NO3 with condensed aromatics. *Pyrene*: mainly 1-nitro-pyrene but also 1,3-, 1,6- and 1,8-dinitropyrene in the particle phase (Kwamena and Abbatt (2008), Zhang et al., (2011), Lui et al (2012), Zhang et al., (2014); Cochran et al., (2016)) with HNO3 and NO2 released into the gas-phase (Gross and Bertram, 2008). *Benzo[a]anthracene*: 7-nitrobenzo[a]anthracene, benzo[a]anthracene-7,12-dione (Zhang et al., 2011; Lui et al., 2012). *Fluoranthene*: 2-nitro-fluoranthene Zhang et al., (2014). *Chrysene*: 6-nitrochrysene and dinitrochyrsene (Lui et al., 2012). *Benz[a]pyrene*: nitrated benz[a]pyrene (Lu et al., 2011). *Anthracene*: 9-Nitro-anthracene (Zhang et al., 2011; Kwamena and Abbatt, 2008; Cochran et al., 2016). *Phananthrene*: mono-nitrophenanthracenes and hydroxynitrates of phenanthrene (Zhang et al., 2011). *Carbaryl*: Initial product is (nitro-1-naphthyl) M-methylcarbamate with dinitro-1-naphthyl)N-methylcarbamate, (hydroxy-1-naphthyl)N-methylcarbamate and (hydroxy-nitro-1-naphthyl)N-methylcarbamate formed in secondary steps (Yang et al., 2011). *Triphenylene*: 1-nitroreiphenylene (major) and 2-nitrotriphenylene, (Zhang et al., 2011).

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