

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

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### NO<sub>3</sub> + aromatics

#### Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
$\gamma_0$			
> 0.1 (pyrene)	293	Mak et al., 2007	CWFT-CIMS (a)
$0.38^{+0.62}_{-0.3}$ (pyrene)	273	Gross and Bertram, (2008)	CWFT-CIMS (b)
$0.79^{+0.21}_{-0.67}$ (pyrene)	293 - 297		
$0.059^{+0.11}_{-0.049}$ (benz[a]anthracene)	273		
$0.13^{+0.53}_{-0.096}$ (benz[a]anthracene)	293 - 297		
$0.087^{+0.28}_{-0.063}$ (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 C<sub>16</sub>H<sub>10</sub> (benzo[def]phenanthrene), benz[a]anthracene is C<sub>18</sub>H<sub>12</sub>, Fluoranthene is C<sub>16</sub>H<sub>10</sub>, nitroguaiacol (C<sub>7</sub>H<sub>7</sub>NO<sub>4</sub>) is 2-methoxy-5-nitrophenol, chrysene (C<sub>18</sub>H<sub>12</sub>) is 1,2-Benzophenanthrene.

#### Comments

- NO<sub>3</sub> ( $7-40 \times 10^{10}$  molecule cm<sup>-3</sup>) was formed by the thermal dissociation of N<sub>2</sub>O<sub>5</sub> and detected following ionisation by I. Pyrene surfaces were solid.
- NO<sub>3</sub> ( $3-37 \times 10^{10}$  molecule cm<sup>-3</sup>) was formed by the thermal dissociation of N<sub>2</sub>O<sub>5</sub> and detected following ionisation by I. Pyrene surfaces were solid. The initial values of  $\gamma$  listed decreased with exposure to NO<sub>3</sub> for samples at 263 K. This effect was greatly reduced for benz[a]anthracene, and absent for pyrene and fluoranthene at 297 K.
- NO<sub>3</sub> ( $4-300 \times 10^9$  molecule cm<sup>-3</sup>) was formed by the thermal dissociation of N<sub>2</sub>O<sub>5</sub> and detected following ionisation by I. The larger values of  $\gamma_0$  were obtained when using low NO<sub>3</sub> concentrations.
- NO<sub>3</sub> present in equilibrium mixtures of NO<sub>2</sub>-NO<sub>3</sub>-N<sub>2</sub>O<sub>5</sub>. Aromatics present as coatings on an azelaic acid particle. Relative loss rate of aromatic (particle) and isoprene (g) monitored to derive  $\gamma$ . Correction for the diffusive limitation to the uptake was achieved by normalising to  $\gamma$  obtained by (Gross and Bertram, 2008) and (Mak et al., 2007).

### Preferred Values

Parameter	Value	T/K
$\alpha_b$	1	
$k_b$ ( $M^{-1} s^{-1}$ )	$3 \times 10^8$	280-300
<i>Reliability</i>		
$\Delta \log(k_b)$	0.5	

#### *Comments on Preferred Values*

Early work (Pitts et al., 1985) on  $NO_3 / N_2O_5$  interactions with pyrene assigned product formation to reaction with  $N_2O_5$  and found no evidence for reaction with perylene. Subsequent research has shown that  $NO_3$  is taken up efficiently to several aromatics, with  $\gamma$  generally between 0.1 and 1.

If the reaction between  $NO_3$  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

$$\gamma = \left\{ \frac{1}{\alpha_b} + \frac{\bar{c}}{4HRT \sqrt{\sum (k_{b(i)} [HC]_{(i)} D_i)}} \right\}^{-1}$$

Where  $k_{b(i)}$  is the liquid-phase rate coefficient for reaction of  $NO_3$  with organic species (i) with concentration  $[HC]$ ,  $D_i$  its diffusion coefficient through the organic matrix and  $H$  its solubility.

A rough estimate for a generic uptake coefficient for  $NO_3$  uptake to aromatics can be made using  $k_b = 3 \times 10^8 M^{-1} s^{-1}$  (equivalent to a gas-phase rate constant of  $5 \times 10^{-13} cm^3 molecule^{-1} s^{-1}$ ),  $D_i = 2 \times 10^{-5} cm^2 s^{-1}$ , and  $H = 0.8 Matm^{-1}$ , this expression results in a value of  $\gamma = 0.3$ , 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  $D_i$  is taken into account by assigning a large uncertainty to  $k_b$ .

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  $D_i$ . For unreactive or very small particles a correction for the diffusio-reactive length may be important (see guide to datasheets), whereas for very reactive particles, the reaction may 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  $NO_3$  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  $NO_3$  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  $HNO_3$  and  $NO_2$  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 dinitrochrysene (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). *Phenanthrene*: mono-nitrophenanthrenes 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-nitrotriphenylene (major) and 2-nitrotriphenylene, (Zhang et al., 2011).

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