IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation - Data Sheet Het_Org4

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NO_3 + unsaturated acids

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
γ_0			
$(7.9 \pm 1.2) \times 10^{-3}$ (linoleic acid, conj.)	273	Moise et al., 2002	CWFT-AS (a)
$(15.0 \pm 2.0) \times 10^{-3}$ (linoleic acid, unconj.)	288		
> 0.12 (linoleic acid, conj.)	278-298	Gross et al., 2009	CWFT-CIMS (b)
> 0.13 (linoleic acid, unconj.)	288		
> 0.07 (oleic acid)	285-302		
1.01 ± 0.18 (linoleic acid, conj.)	295	Zhao et al., 2011	AFT (c)
0.53 ± 0.12 (linoleic acid, unconj.)	295		
0.27 ± 0.06 (oleic acid, conj.)	295		
0.72 ± 0.17 (linolenic acid, conj.)	295		
$(2\text{-}6) \times 10^{-3}$ (abietic)	298	Knopf et al., 2011	CWFT-CIMS (d)
$0.4^{+0.45}_{-0.31}$ (linoleic)	298		
$0.29^{+0.71}_{-0.21}$ (oleic)	298		
0.14 ± 0.03 (oleic)	RT	Renbaum-Wolff and Smith, (2012)	AFT (e)

Abietic acid ($C_{20}H_{30}O_2$) is Abieta-7,13-dien-18-oic acid, Linoleic acid is $C_{18}H_{32}O_2$ ((9*Z*,12*Z*)-9,12-octadecadienoic acid), linoleic acid (conj.) is a mixture of cis- and trans-9,11 octadecadienoic acid and -10,12 octadecadienoic acid, linolenic acid is $C_{18}H_{30}O_2$ ((9*Z*,12*Z*,15*Z*)-9,12,15-octadecatrienoic acid), oleic acid is $C_{18}H_{34}O_2$, ((9*Z*)-Octadec-9-enoic acid), RT = room temperature.

Comments

(a) Rotating, coated wall flow tube. NO_3 ($5\text{-}50 \times 10^{11}$ molecule cm^{-3}) was formed by the thermal dissociation of N_2O_5 and detected by diode laser absorption at 662 nm.

(b) Rotating, coated wall flow tube. NO_3 ($3.5\text{-}16 \times 10^{10}$ molecule cm^{-3}) was formed by the thermal dissociation of N_2O_5 and detected following ionisation by I^-. The uptake coefficient for diethyl sebacate decreased to ~0.06 ± 0.015 upon freezing at 268-283 K.

(c) Mixed-phase, relative rates method. Loss of particle-phase organic monitored relative to loss of gas-phase reference reactant (isoprene, 2,3,-dimethyl-1,3-butadiene, cyclopentane and 2-methyl-2-2butene).

(d) NO_3 ($4\text{-}300 \times 10^9$ molecule cm^{-3}) was formed by the thermal dissociation of N_2O_5 and detected following ionisation by I^-. The larger values of γ_0 were obtained when using low NO_3 concentrations.

(e) Mixed-phase, relative rates method. NO_3 generated from 355 nm photolysis of a mixture of HONO / HNO_3. Particle-phase oleic acid and gas-phase isoprene (reference reactant) monitored by Aerosol CIMS.

Preferred Values

Parameter	Value	T/K
α_b	1	
k_b (M^{-1} s^{-1})	3×10^8	280-300

Reliability

$\Delta \log (k_b)$	0.5

Comments on Preferred Values

There is considerable scatter in the uptake coefficients obtained for different unsaturated acids and also when comparing results of different groups for the same acid (e.g. linoleic). Good agreement between expeirments using bulk samples and particlulate linoleic and oleic acids suggest that the uptake coefficient is > 0.2.

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:

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

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

A rough estimate for a generic uptake coefficient for NO_3 uptake to unsaturated acids can be made using $k_b = 3 \times 10^8$ M^{-1} s^{-1} (equivalent to a gas-phase rate constant of 5×10^{-13} cm^3 $molecule^{-1}$ s^{-1}), D_l, $= 2 \times 10^{-5}$ 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_l 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_l. 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 NO_3 concentration- and time-dependence of the uptake coefficient to a sample of abeitic acid (Knopf et al., 2011) could be described with a multilayer model of surface and bulk reactions and bulk diffusion of NO_3 (Shiraiwa et al., 2012).

The reaction of NO_3 with the unsaturated organics considered here proceeds largely through addition. Products from the reaction of NO_3 with oleic acid are carboxylic acids including hydroxy nitrates, carbonyl nitrates, dinitrates and hydroxydinitrates (Hung et al., 2005; Docherty and Ziemann, 2006; Zhao et al., 2011).

References

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