NO_3 + saturated alcohols / carbonyls

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
γ_0			
$(2.1 \pm 0.3) \times 10^{-3}$ (n-octanoic acid)	290	Moise et al., 2002	CWFT-AS (a)
$(7.1 \pm 1.6) \times 10^{-3}$ (1-octanol)	258		
$(0.8 - 1.7) \times 10^{-3}$ (glycerol)	268-293	Gross et al., 2009	CWFT-CIMS (b)
$(3.5 - 4.5) \times 10^{-3}$ (diethyl sebacate)	278-298		
$(4.4 \pm 0.4) \times 10^{-3}$ (diethyl sebacate)	278	Xiao and Bertram, 2011	CWFT-CIMS (b)
$(3.9 \pm 0.3) \times 10^{-3}$ (dioctyl sebacate)	278		
$(16 \pm 8) \times 10^{-3}$ (tridecanal)	263	Iannone et al., 2011	CWFT-CIMS (c)
$0-12 \times 10^{-3}$ (tridecanal in organic matrix)	275		
$(1-3) \times 10^{-3}$ (levoglucosan)	298	Knopf et al., 2011	CWFT-CIMS (d)
$(6 \pm 1) \times 10^{-3}$ (16-mercapto-1-hexadecanol, SAM)	RT	Zhang and Morris, 2015	RAIRS (e)

diethyl sebacate is $C_2H_5OC(O)(CH_2)_8C(O)OC_2H_5$), dioctyl sebacate is $(CH_2)_8(C(O)OC_8H_{17})_2)$, Levoglucosan $(C_6H_{10}O_5)$ is (1R,2S,3S,4R,5R)-6,8-Dioxabicyclo[3.2.1]octane-2,3,4-triol. RT = room temperature.

Comments

(a) Rotating, coated wall flow tube. NO_3 (5-50 $\times$ 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 (3.5-16 $\times$ 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 by a factor ~10 upon freezing.

(c) NO_3 (3.6-8.5 $\times$ 10^{11} molecule cm^{-3}) was formed by the thermal dissociation of N_2O_5 and detected following ionisation by I$^-$. Tridecanal was solid at 263 K or was dissolved in diethyl sebacate, dioctyl sebacate or squalane for experiments at 275 K.

(d) NO_3 (4-300 $\times$ 10^9 molecule cm^{-3}) was formed by the thermal dissociation of N_2O_5 and detected following ionisation by I$^-$. The higher values of γ were obtain at lowest NO_3 concentrations. Levoglucosan was solid at the experimental temperature.

(e) γ derived by observing loss rate of terminal hydroxyl groups and calculating surface-near NO_3 concentratons.

<div align="center">

Preferred Values

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Parameter	Value	T/K
α_b	1	
k_b (M^{-1} s^{-1})	6×10^4	270-300

Reliability

$\Delta \log (k_b)$	0.6

Comments on Preferred Values

Uptake to liquid saturated alcohols and carbonyls is relatively slow with uptake coefficients between 10^{-3} and 10^{-2}. The highest values are obtained with organics that also are expected to have more rapid gas-phase reactions with NO$_3$ (e.g. aldehydes).

The uptake coefficients for n-octanoic acid, 1-octanol and diethyl sebacate decreased significantly when the surface was frozen at lower temperatures, which was attributed to the reduced rate of diffusion of NO$_3$ into the bulk sample (Moise et al., 2002; Gross et al., 2009). In addition, γ for glycerol is lower than expected given trends in gas-phase reactivity and this is also attributed to its high viscosity limiting diffusion through the bulk sample (Gross et al., 2009). Iannone et al (2011) showed that the uptake coefficient for NO$_3$ reacting with tridecanal depended on its concentration and on the matrix organic with values of $H\sqrt{k_{bi}D_l}$ of 9.4, 6.9 and 3.6 cm M$^{0.5}$ atm^{-1} s^{-1} for NO$_3$ uptake and reaction with tridecanal in DES, DOS and squalane, respectively.

Thus, if the reaction between NO$_3$ and the saturated alcohol / carbonyl (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 saturated alcohols or carbonyls can be made using $k_b = 6 \times 10^4$ M^{-1} s^{-1} (equivalent to a gas-phase rate constant of 1×10^{-16} 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 $\gamma = 5 \times 10^{-3}$, 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 levoglucosan 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 saturated organics considered here proceeds largely through abstraction. Zhang and Morris (2015) observed formation of organic nitrates simultaneously with loss of terminal CH$_2$OH groups and concluded that reaction proceeds via abstraction at terminal –CH$_2$OH group.

References

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