NO_3 + alkanes

Experimental data

Parameter	Temp./K	Reference	Technique/ Comments
γ_0			
$(2.6 \pm 0.8) \times 10^{-3}$ (n-hexadecane)	293	Moise et al., 2002	CWFT-AS (a)
$(14 \pm 2) \times 10^{-3}$ (n-hexadecane, SAM)	293	Knopf et al. 2006	CWFT-CIMS (b)
$(8.8 \pm 2.5) \times 10^{-4}$ (octadecanethiol, SAM)	298		
$(5.2 \pm 0.4) \times 10^{-3}$ (squalane)	278	Xiao and Bertram, 2011	CWFT- CIMS (c)
$< 7.8 \times 10^{-3}$ (squalane)	293	Lee et al., 2013	AFT −AMS (d)
$(2.1 \pm 0.8) \times 10^{-3}$ (heptamethylnonane)	253	Moise et al., 2002	CWFT-AS (a)

Squalane is $C_{30}H_{62}$ (2,6,10,15,19,23-Hexamethyltetracosane). SAM = self-assembled monolayer.

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) Coated wall flow tube with n-hexadecane or octadecanethiol present as self-assembeld monolayers. NO_3 (2-4 $\times 10^{11}$ molecule cm^{-3}) was formed by the thermal dissociation of N_2O_5 and detected following ionisation by I^-.

(c) NO_3 (3-16 $\times 10^{10}$ molecule cm^{-3}) was formed by the thermal dissociation of N_2O_5 and detected following ionisation by I^-.

(d) ~ 100 nm particles of squalane. Measurements performed using a mixture of NO_3 and N_2O_5, with N_2O_5 monitored as NO_2 following thermal dissociation. The uptake coefficient for NO_3 reacting with the squalane was calculated assuming no heterogeneous loss of N_2O_5 and is thus an upper limit.

Preferred Values

Parameter	Value	T/K
α_b	1	
k_b ($M^{-1} s^{-1}$)	6×10^4	280 - 300

Reliability

$\Delta \log (k_b)$	0.7	

Comments on Preferred Values

Uptake to liquid saturated hydrocarbons is relatively slow with initial uptake coefficients between 10^{-3} and 10^{-2}. Moise et al (Moise et al., 2002) found that (for a solid sample) uptake to a branched chain alkane was more efficient than for a branched alkane, which is consistent with known trends in gas-phase reactivity of NO_3. The uptake coefficient 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.

If the reaction between NO_3 and the alkane (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), 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 an alkane can be made using $k_b = 6 \times 10^4$ M^{-1} s^{-1} which is 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 results in a value of $\gamma = 5 \times 10^{-3}$, which is consistent with the experimental data within the uncertainty assigned to k_b. 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.

In their experiments on octadecanethiol, Knopf et al. (2006) observed formation of condensed phase carbonyl species and no evidence for significant volatilisation of the organic substrate. In further experiments, the same group (Gross and Bertram, 2009) observed formation of organonitrate products for the same alkane. In contrast, gas-phase product analysis in the experiments of Lee et al. (2013) on squalene showed that NO_3 was converted stoichiometrically to NO_2.

References

Gross, S. and Bertram, A. K.: J. Geophys. Res. 114, D02307, doi: 10.1029/2008JD010987, 2009.

Knopf, D. A., Mak, J., Gross, S. and Bertram, A. K.: Geophys. Res. Lett. 33, 2006.

Moise, T., Talukdar, R. K., Frost, G. J., Fox, R. W. and Rudich, Y.: J. Geophys. Res.-Atmos. 107, D2, doi: 10.1029/2001JD000334, 2002.

Xiao, S., and Bertram, A.K.: Phys. Chem. Chem. Phys. 13, 6628-6636, 2011.