NO_3 + alkenes

Experimental data

Parameter	Temp./K	Reference	Technique/Comments
γ_0			
$(1.6 \pm 0.3) \times 10^{-3}$ (1-octadecene)	293	Moise et al., 2002	CWFT-AS (a)
$(2.3 \pm 0.9) \times 10^{-3}$ (1-hexadecene)	277		
$(5.8 \pm 2.0) \times 10^{-3}$ (7-tetradecene)	246		
$(34^{+44}_{-18}) \times 10^{-3}$ (undec-10-ene-1-thiol, SAM)	298	Gross and Bertram, 2009	CWFT-CIMS (b)
$(140^{+860}_{-50}) \times 10^{-3}$ (methyl oleate)	278	Xiao and Bertram, 2011	CWFT-CIMS (c)
$(180 \pm 30) \times 10^{-3}$ (squalene)	293	Lee et al., 2013	AFT-AMS (d)
$(2.3 \pm 0.5) \times 10^{-3}$ (17-octadecene-1-thiol, SAM)	RT	Zhang et al., 2014	RAIRS (e)

RT = room temperature, squalene is $C_{30}H_{62}$ (2,6,10,15,19,23-Hexamethyltetracosane),
methyl oleate is $CH_3(CH_2)_7CH=CH(CH_2)_7CO_2CH_3$

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) NO_3 (1-2 $\times 10^{11}$ 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^-. The uptake coefficient decreased by a factor of 10 following surface exposure to NO_3 for 90 mins.

(d) ~ 100 nm particles of squalene. 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 squalene was calculated assuming no heterogeneous loss of N_2O_5.

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

Preferred Values

Parameter	Value	T/K
α_b	1	
k_b ($M^{-1} s^{-1}$)	1.2×10^6	270 - 300

Reliability

$\Delta \log (k_b)$	1	

Comments on Preferred Values

NO$_3$ adds to double bonds and the experimentally derived uptake coefficient for NO$_3$ reacting with alkenes varies by ~ two orders of magnitude, with the largest values obtained with squalene (six double bonds) (Lee et al., 2013). Lee et al. (2013) report that the uptake coefficient increased with exposure time (to 0.8 ± 0.1) indicating that the nitrated products are more reactive to NO$_3$ than squalene itself. In contrast, both Gross and Bertram (2009) and Zhang et al. (2014) found that γ decreased with exposure as vinyl groups were consumed.

Gross and Bertram (2009) suggest that the larger γ_0 values they get for undec-10-ene-1-thiol (a SAM with a terminal, single double-bond) compared to values reported by Moise et al. (2002) for liquid alkenes, with a single double-bond may be due to the location of the (reactive) double-bond at the gas-surface interface. The very high value of γ_0 for methyl-oleate, may partially reflect the high electron density around the double bond of the branched alkene.

Xiao and Bertram (2011) investigated the uptake of NO$_3$ to methyl oleate in binary mixtures of less reactive, saturated organics such as squalane, diethyl sebacate (DES) and dioctyl sebacate (DOS). The results could be described by the usual resistor model:

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

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.

Xiao et al derived values of $H\sqrt{k_{bi}D_l}$ of 69.4, 35.4 and 26.1 cm M$^{0.5}$ atm^{-1} s^{-1} for NO$_3$ uptake and reaction with methyl oleate in DES, DOS and squalane, respectively. The lower values indicate that the diffusion term (D_l) influences the uptake coefficient significantly.

A rough estimate for a generic uptake coefficient for NO$_3$ uptake to an alkene can be made by using $k_b = 1.2 \times 10^6$ M^{-1} s^{-1} which is equivalent to a gas-phase rate constant of 2×10^{-15} 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 $\gamma = 2 \times 10^{-2}$, which is consistent with the experimental data if we assign a total uncertainty of a factor 10. 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 $k_{b(i)}[\text{HC}]_{(i)}$ 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.

Lee et al found that ~ 1.5 squalene molecules were reacted per NO$_3$ taken up, indicating that secondary consumption of squalene was operative and that, under their conditions of concentration and exposure time up to three NO$_3$ subunits added to the squalene backbone during reaction. The formation of consensed-phase organonitrates and carbonyls has also been documented (Gross et al., 2009; Zhang et al. (2014).

References

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