

2.2 Nitrogen oxides chemistry

Common acronyms for nitrogen compounds:

N(-III) = $\text{NH}_4^+ + \text{NH}_3$, total reduced nitrogen‘

N(V) = $\text{NO}_3^- + \text{HNO}_3$

IN = ,inorganic nitrogen‘

ON (or AON) = (atmospheric) organic nitrogen‘

$\text{NO}_x = \text{NO} + \text{NO}_2$, nitrogen oxides‘

$\text{NO}_y = \text{NO}_x + \text{N(V)} + \text{NO}_3 + \text{N}_2\text{O}_5 + \text{HNO}_2 + \text{HNO}_4 + \text{PAN}$
= total oxidized nitrogen

$\text{NO}_z = \text{NO}_y - \text{NO}_x$

PAN = $\text{CH}_3\text{C(O)OOONO}_2$, peroxyacetyl nitrate

PPN = $\text{CH}_3\text{CH}_2\text{C(O)OOONO}_2$, peroxypropionyl nitrate

Not included: N_2O nitrous oxide

2.2.1 Nitric oxide chemistry

Aliphatic nitrites



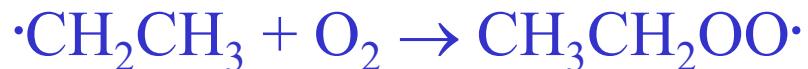
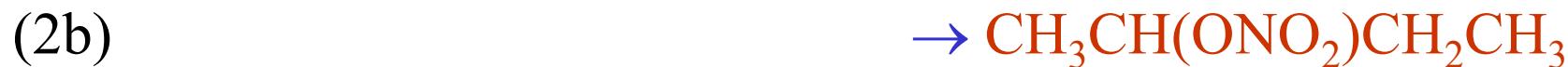
aliphatic nitrite (*rarely stable*)

Aliphatic nitrates



aliphatic nitrate (*secondary channel*)

NO chemistry: nitrates formed from alkanes, example butane



$k_{2b}/(k_{2a} + k_{2b})$:	1-butyl	0.04
	2-butyl	0.08
	1-pentyl	0.06
	2-pentyl	0.13
	3-pentyl	0.12
	tert-butyl	0.18
	2-hexyl	0.22
	2-heptyl	0.32
	2-octyl	0.35

Black forest 1990-91:

$0.03\text{-}0.6 \text{ ppbv } \text{CH}_3(\text{CH}_2)_{0\text{-}7}\text{ONO}_2$

RONO₂ contribution to total oxidants:

$\text{CH}_3(\text{CH}_2)_{0\text{-}7}\text{ONO}_2 \approx 0.004 * \text{O}_x$

(Flocke et al., 1998)

2.2.2 Nitrogen dioxide chemistry

2.2.2.1 Reaction with OH and HO₂

OH: Nitric acid



$\rightarrow 3.3 \text{ Acids}$

HO_2 : Pernitric acid HOONO_2 – relevant in the upper troposphere



$$K_{1,0} = 1.8 \times 10^{-31} |x_{\text{N}_2}| (T/300)^{-3.2} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$K_{1,\infty} = 4.7 \times 10^{-12} (T/300)^{-1.4} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}; F_c = 0.6$$

$$K_{-1,0} = 4.1 \times 10^{-5} |x_{\text{N}_2}| e^{-10650/T} \text{ s}^{-1}$$

$$K_{-1,\infty} = 4.8 \times 10^{15} |x_{\text{N}_2}| e^{-11170/T} \text{ s}^{-1}; F_c = 0.6$$

(kinetic data taken from Atkinson et al., 2004)

Examples	T (K)	p (hPa)	h (km)	τ (HNO_4)	$\mu(\text{NO}_2)$ (nmol/mol)	$\mu(\text{HO}_2)$ (pmol/mol)	$\mu(\text{HNO}_4)$ (pmol/mol)
	230	300	9	6 d	0.01	1	54
					0.05	1	270
	270	700	3	9 min	0.02	0.4	0.08
					0.2	0.4	0.8
	273	1000	0	5 min	1	3	25
					30	3	750
	293	1000	0	25 s	1	3	1.7
					30	10	165

→ high solubility (acid): changes NO_x phase distribution and residence time

→ NO_x reservoir compound

2.2.2.2 Reactions with hydrocarbons

Direct reaction of NO_2



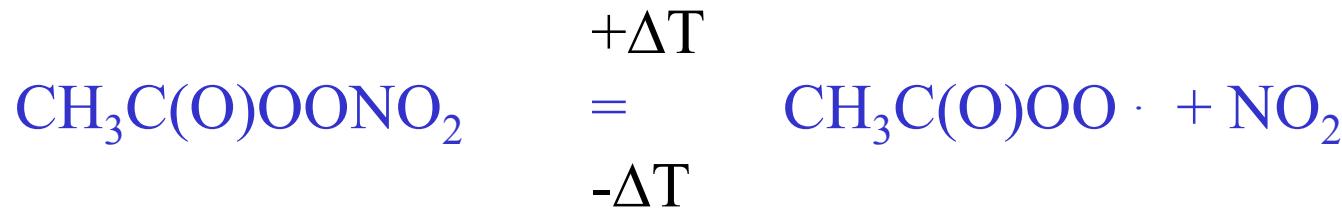
Acyl compounds: ketones, example peroxyacetyl nitrate



...aldehydes, example peroxyacetyl nitrate



Peroxyacetyl nitrate (PAN): thermically labile



$$k = 1.95 \times 10^{16} e^{-13543/T} \text{ s}^{-1};$$

$$\tau = 2a @ 243K$$

$$\tau = 2d @ 273K$$

$$\tau = 45 \text{ min} @ 298 K$$

→ NO_x reservoir compound ↔ changes NO_x effective residence time
→ delayed ozone formation

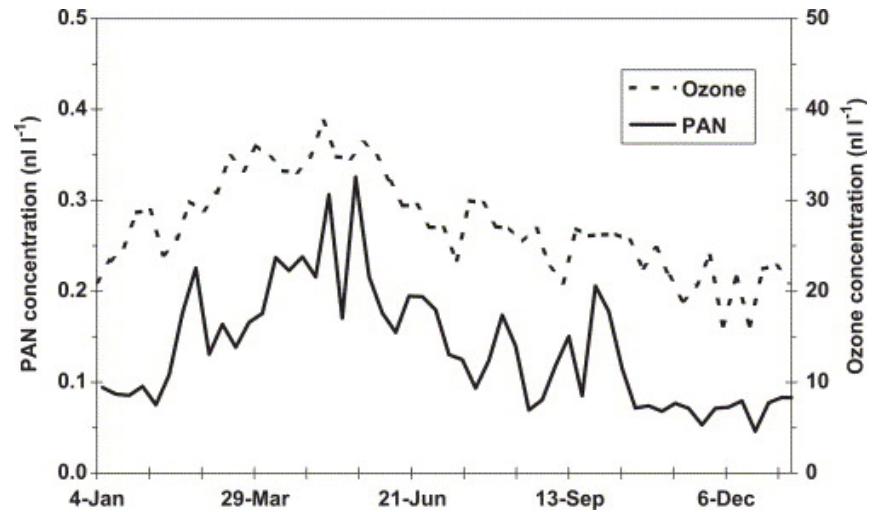
PAN sink reactions:



Distributions - temporal

Peroxyacetyl nitrate - occurrence

- 1) in the cold
- 2) in photochemical smog and in plumes of urban areas



Rural Scotland (McFadyen & Cape, 2005)

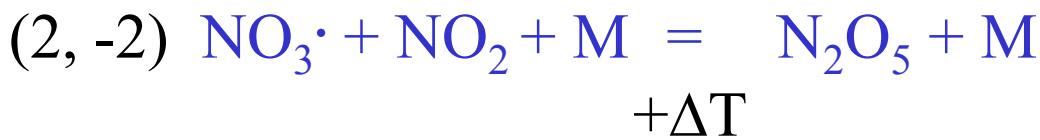
- 3) ... even in plumes of whole regions:

2.2.3 Nitrate radical

NO₂ oxidation by ozone: NO₃ formation
The adduct N₂O₅ – a thermically labile NO₃ reservoir



$$-\Delta T$$



$$K_{2,0} = 3.6 \times 10^{-30} |x_{\text{N}_2}| (T/300)^{-4.1} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

$$K_{2,\infty} = 1.9 \times 10^{-12} (T/300)^{-0.2} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}; F_c = 0.35$$

$$K_{-2,0} = 1.3 \times 10^{-3} |x_{\text{N}_2}| (T/300)^{-3.5} e^{-11000/T} \text{ s}^{-1}$$

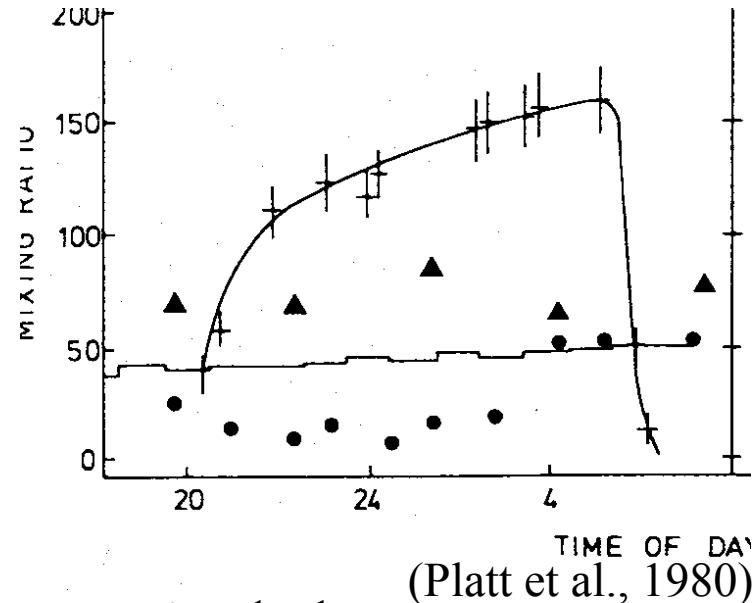
$$K_{-2,\infty} = 6.2 \times 10^{14} (T/300)^{-0.2} e^{-11000/T} \text{ s}^{-1}; F_c = 0.35$$

(kinetic data taken from Atkinson et al., 2004)

Equilibrium:

$$c_{\text{N}_2\text{O}_5} / (c_{\text{NO}_2} c_{\text{NO}_3}) = K = k_2 / k_{-2}$$

→ N₂O₅ not measurable, but can be inferred from c_{NO₂} and c_{NO₃}

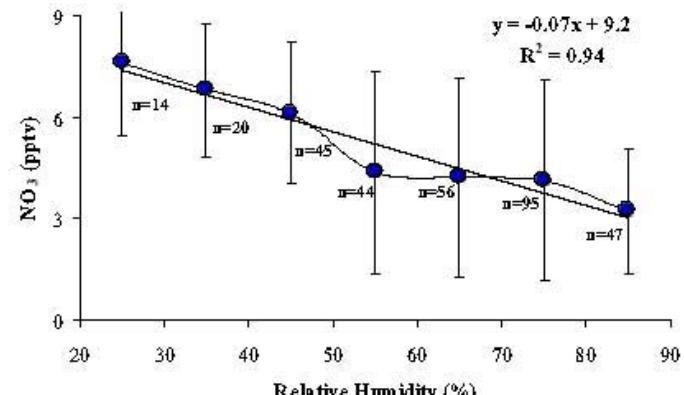
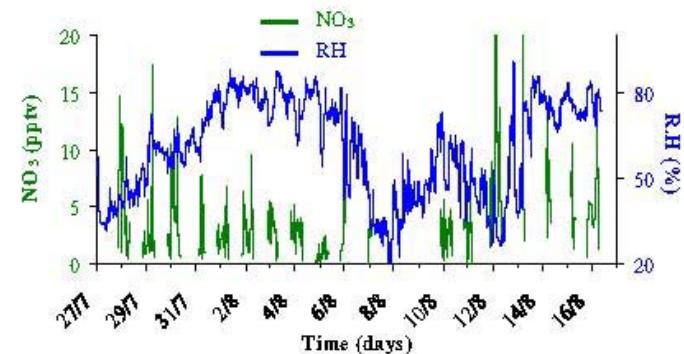
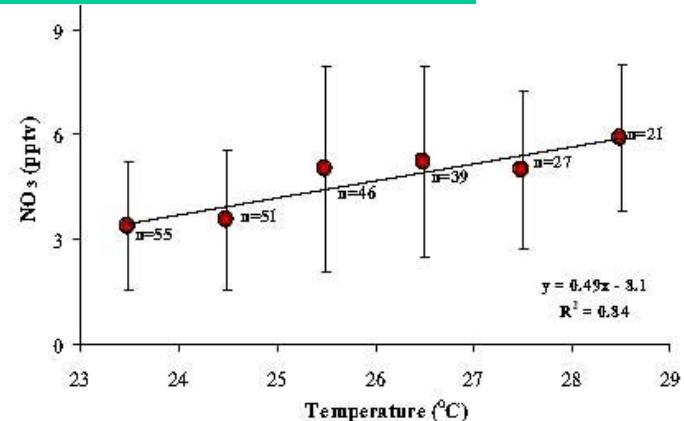


(Platt et al., 1980)

Nitrate radical

Observations of NO_3 radicals in the boundary layer

Site	Coordinates	NO_3 Average (pptv)	NO_3 Maximum (pptv)	Total path (km)	Year (summer)	Ref.
Continental Boundary Layer						
Lindenberg	52°13'N- 14°07'E	4.6	85	10	1998	Geyer et al., 2001
Marine Boundary Layer						
Tenerife	28°40'N- 16°05'W	8	20	9.6	1994	Carslaw et al., 1997
Kap Arkona (Rugen Island)	54°30'N- 13°30'E	6 - 10	98	7.3	1993/94	Heintz et al., 1996
Wayborne Clean conditions	52°57'N- 1°08'E	6	-	5	1995	Allan et al., 1999
Mace Head	53°19'N, 9°54'W	5	40	8.4	1996	Allan et al., 2000
Finokalia	35°30'N, 25°7'E	4.5	37	10.4	2001	This work

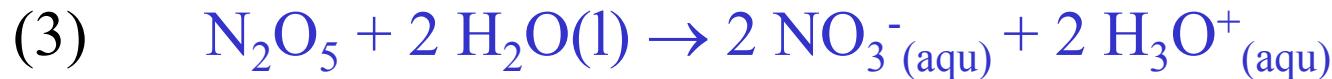
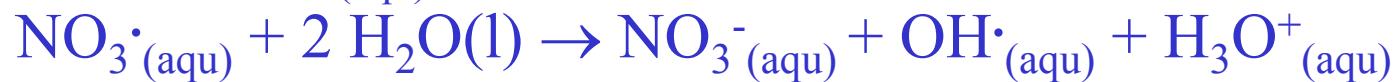


Source: Thermically labile equilibrium with N_2O_5
 Sinks: Aerosol particles, droplets
 Reactions with hydrocarbons

Nitrate radical - sinks

Day-time: Rapid photolysis of NO_3

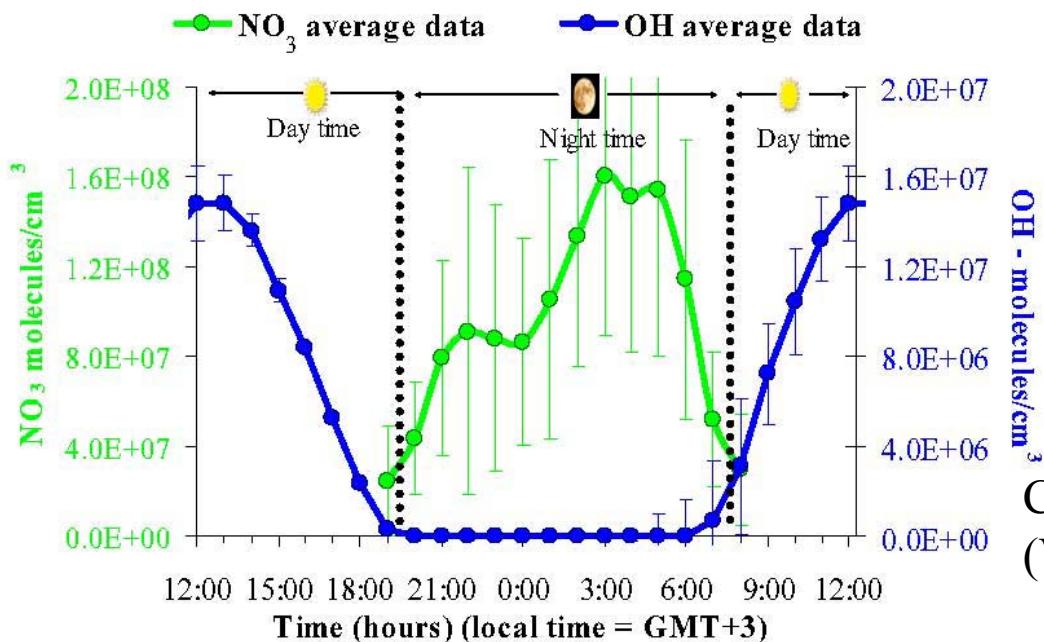
in clouds, on wet particles:



Examples	r.h.	μ_{NO_2}	μ_{NO_3}	$\tau_{\text{NO}_3}^{\text{het}}$	$\tau_{\text{N}_2\text{O}_5}^{\text{het}}$	Yield OH (%)	Production $\frac{dc_{\text{OH}(\text{aq})}}{dt}$ (molec $\text{cm}^{-3} \text{s}^{-1}$)
	(%)	(nmol /mol)	(nmol /mol)	(s)	(s)	(%)	
Marit. aerosol	60	1	0.042	1960	1890	8.0	9.1×10^4
	90	1	0.020	840	320	1.9	4.3×10^4
	60	10	0.42	1960	1890	8.0	9.1×10^5
	90	10	0.20	840	320	1.9	4.3×10^5
Continental aerosol	60	10	0.90	5800	4200	3.3	3.2×10^5
	90	10	0.70	4500	3800	1.4	1.2×10^5
Coastal fog	> 96	1	1.8×10^{-5}	24	6.3	0.8	1.9×10^4
Radiation fog	> 96	10	1.1×10^{-5}	14	3.7	0.13	2.0×10^4

Radical distributions - temporal

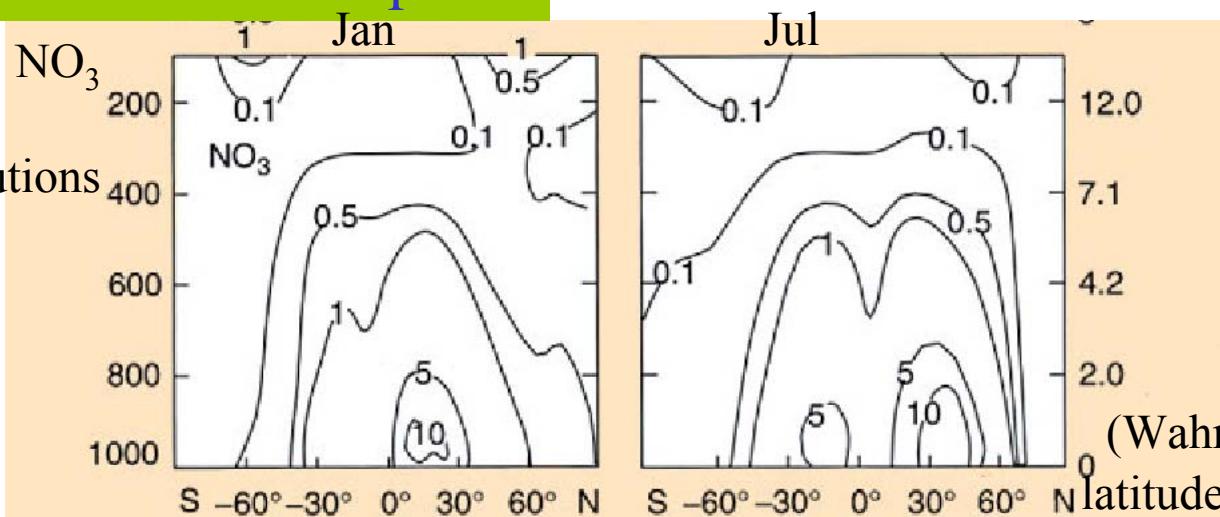
NO₃ chemistry is night chemistry only:
Degradation of hydrocarbons during the night



Crete 2001-03
(Vrekoussis et al., 2006)

Radical distributions - spatial

Zonal distributions



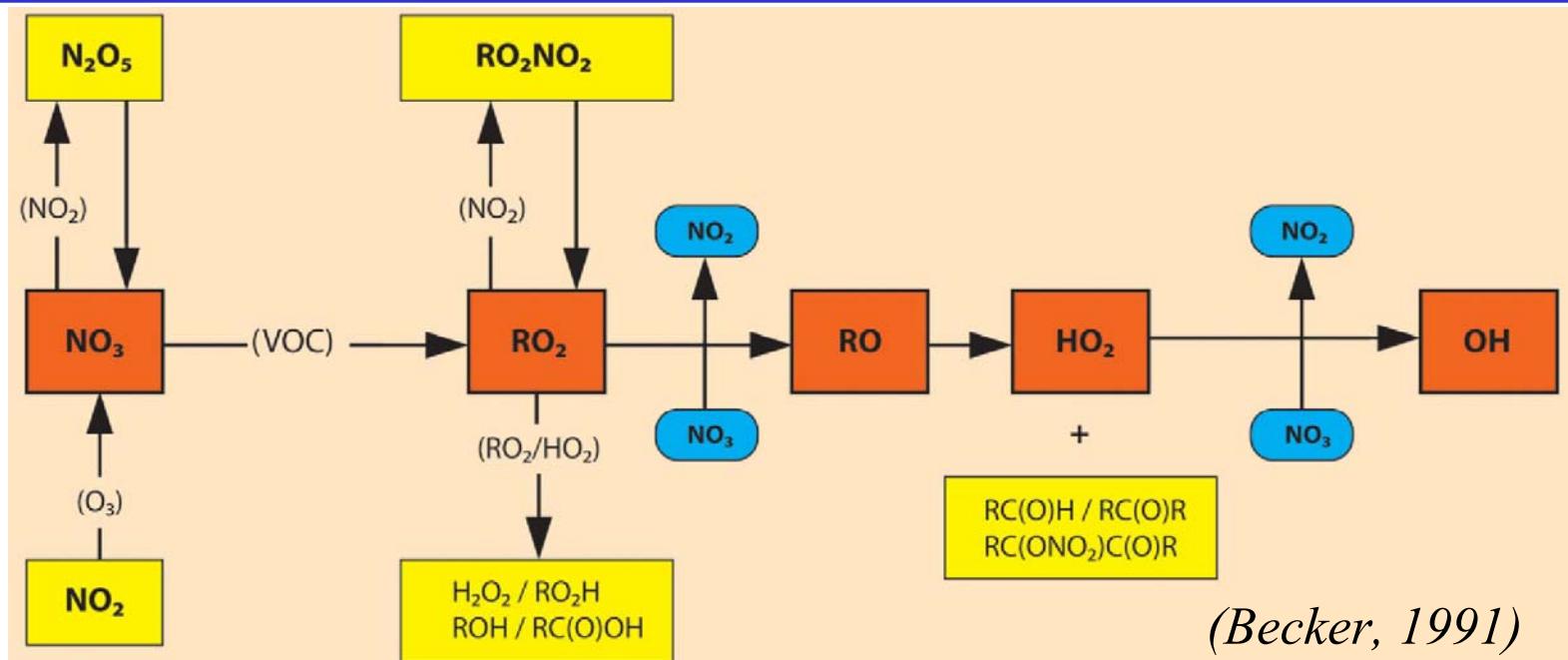
(Wahner & Moortgat, 2007)

NO_3 chemistry: alkanes, example butane

Degradation of hydrocarbons during the night

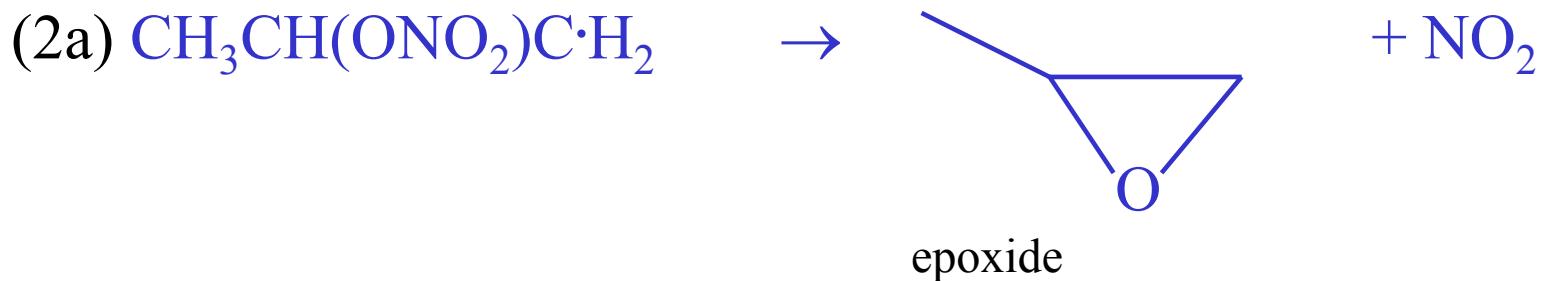
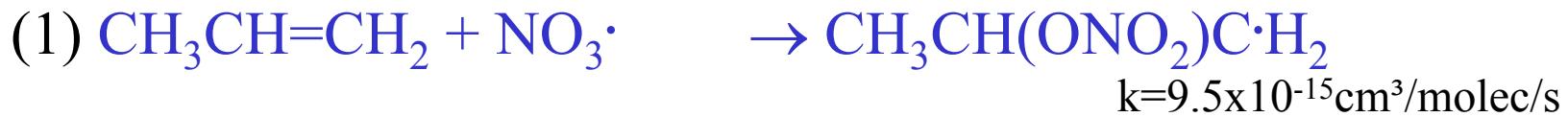


further similar to chemistry after OH attack:



NO₃ chemistry: alkenes, example propene

Preferential is the addition to the higher substituted radical (like OH reaction):



NO_3 reactivity towards hydrocarbons: overview

$$\begin{array}{ll} \text{HC}_x & k_{\text{NO}_3} \\ & 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \end{array}$$

Alkanes:

CH_4	< 0.001
CH_3CH_3	0.0014
$\text{CH}_3\text{CH}_2\text{CH}_3$	0.017
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$	0.046
$\text{CH}_3\text{CH}(\text{CH}_3)_2$	0.11
$\text{CH}_3(\text{CH}_2)_3\text{CH}_3$	0.087

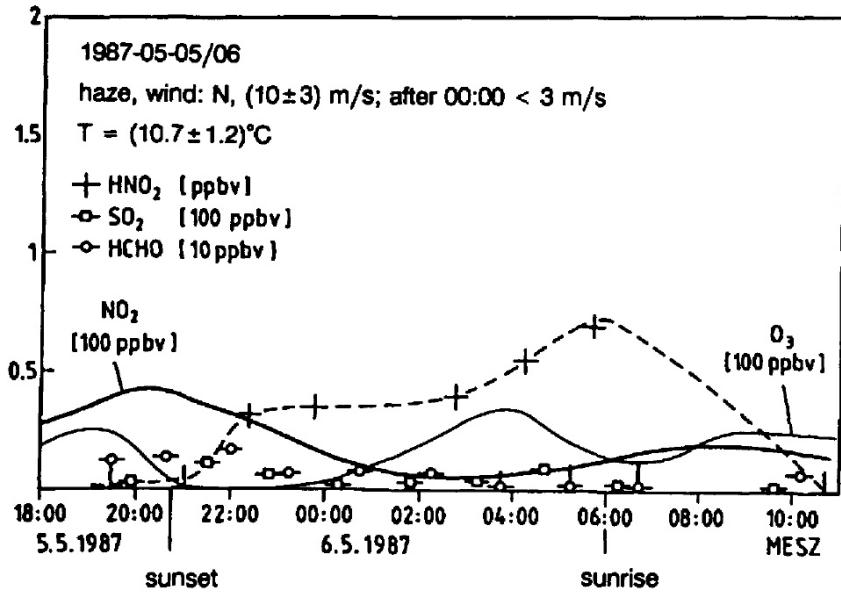
Alkenes:

$\text{CH}_2=\text{CH}_2$	0.21
$\text{CH}_2=\text{CHCH}_3$	9.5
$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	14
cis- $\text{CH}_3\text{CH}=\text{CHCH}_3$	350
trans- $\text{CH}_3\text{CH}=\text{CHCH}_3$	390
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	330
α -pinene	590
β -pinene	210

2.2.4 Nitrous acid

Observations field: night-time accumulation (*Perner & Platt, 1979, besides others*)

Day-time sink: $\text{HNO}_2 + \text{hv}(\lambda=300-405 \text{ nm}) \rightarrow \text{OH} \cdot + \text{NO}$



Urban areas
Rural areas
Remote

$c_{\text{HNO}_2 \text{ max}}$ ($\mu\text{g / m}^3$)	$c_{\text{HNO}_2 \text{ max}} / c_{\text{NO}_2}$ (% mol / mol)
5.2 (1.5 - 21)	4.34 (1.8 - 13)
1.7 (0.4 - 2.5)	3.26 (1.7 - 13)
0.092 (< 0.2 - 0.8)	> 20 (7)

(Lammel & Cape, 1996)

Observations laboratory: radical source in laboratory vessels (‘smog chambers’)
(Pitts et al., 1984, besides others)

Source for HNO₂ in field and laboratory = ?

HNO₂: Significance

Tropospheric chemistry: Efficient radical source, in particular in winter and in high latitudes (before sunrise in the UV)

$$dc_{OH}/dt [\cdot 10^6 / \text{cm}^3/\text{s}] =$$

- from HNO₂ peak 34 ± 6 (09:00h)

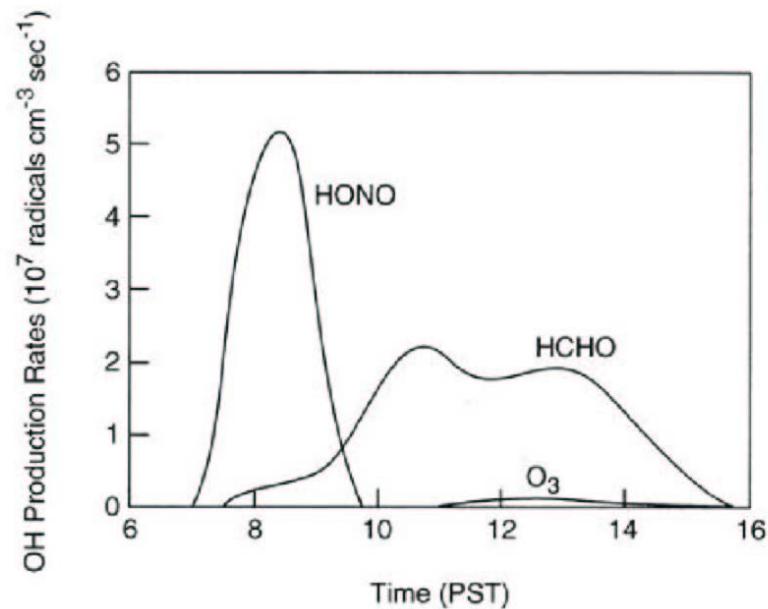
from ozone 23 ± 4 (12:00h)

in urban California (Winer & Biermann, 1994)

- Integral (06:00-18:00 h) from HNO₂ 58 ± 9 ,

HCHO 33 ± 8 , O₃ 38 ± 6

in urban Italy (Acker et al., 2006)



Toxicology:

- Precursor of carcinogenic substances, i.e. nitrosamines, RNHNO

Sources of nitrous acid

1. Direct emission from road traffic: $\approx 0.008 \times \text{NO}$
by far not enough

2. Gas-phase:



3. Heterogeneous reaction (*on surfaces: wall, particles*)



Kinetics:

$$\frac{dc_{\text{HNO}_2}}{dt} = k^{\text{het}} c_{\text{NO}_2} c_{\text{H}_2\text{O}}^a ; a = 0 \text{ or } 1$$

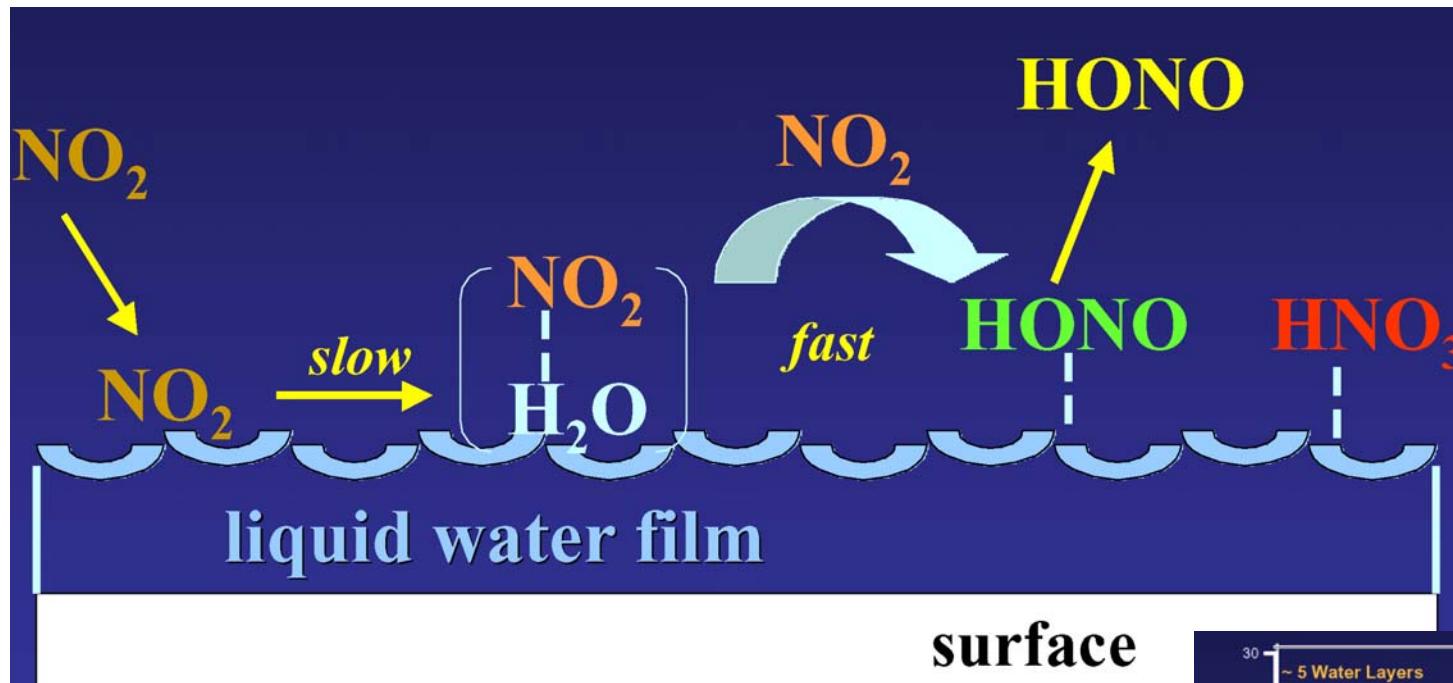
$$k^{\text{het}} = \gamma_i (S/V) \langle v_i \rangle / 4 \approx 1 \times 10^{-20} (S/V) \text{ cm}^4 \text{ molec}^{-1} \text{ s}^{-1}$$

(humid wall; Svensson *et al.*, 1987)

$\gamma_{\text{NO}_2} \approx 0.01$ (Kleffmann *et al.*, 1998)

Dark surface source reaction – water film

Suggested mechanism (in agreement with isotope and kinetic studies):

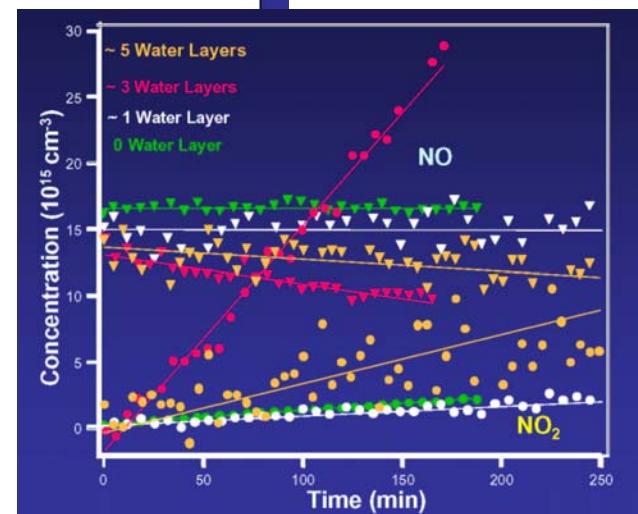


Open questions:

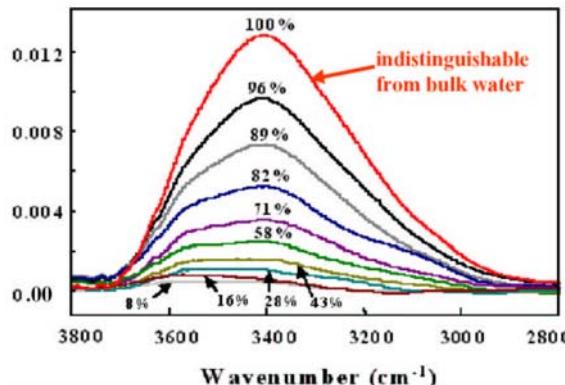
- What means 'surface'
- Are water film molecules bulk liquid ?

Indeed: Kinetics is function of film thickness

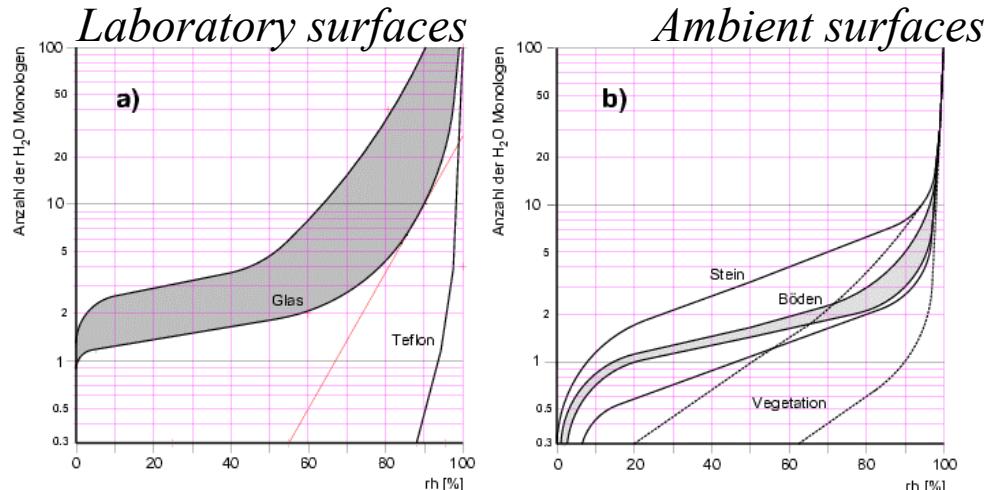
(Lammel, 1996; Saliba et al., 2001)



Dark surface source reaction – water film

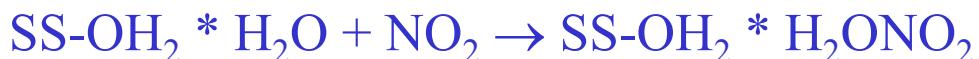
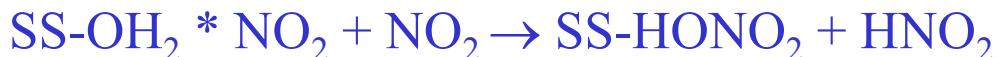
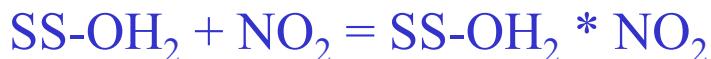


- Shift in band peak to higher wavenumbers (higher energy) → “2 D” water!



Suggested mechanism (in agreement with isotope and kinetic studies):

a)

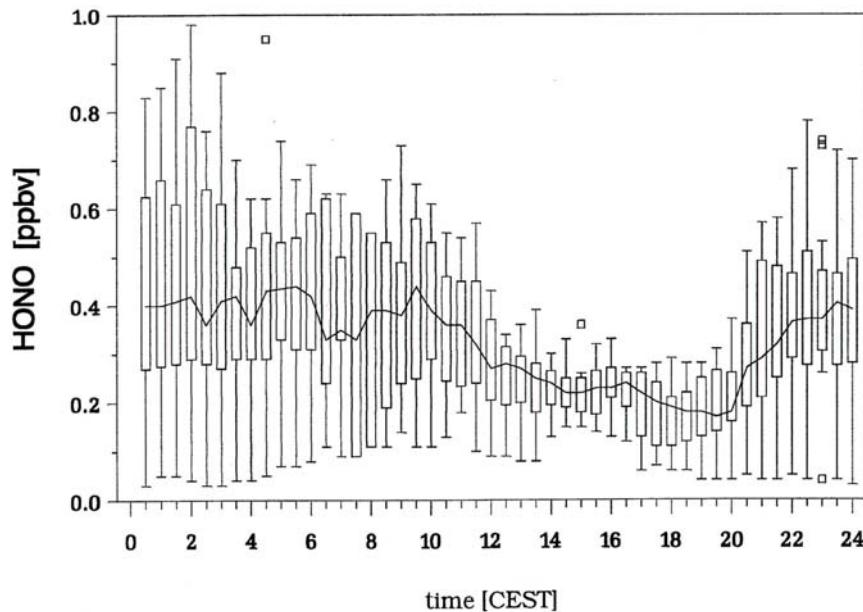


b)



(Lammel, 1996; Saliba et al., 2001; Kleffmann et al., 2003)

Field: strong day-time source



steady state approximation:

$$\frac{dc_{\text{HNO}_2}}{dt} = 0 = -j_{\text{HNO}_2} c_{\text{HNO}_2} - k_{\text{HNO}_2+\text{OH}} c_{\text{OH}} c_{\text{HNO}_2} + k_{\text{NO}+\text{OH}} c_{\text{NO}} c_{\text{OH}}$$
$$c_{\text{HNO}_2} = k_{\text{NO}+\text{OH}} c_{\text{NO}} c_{\text{OH}} / (j_{\text{HNO}_2} + k_{\text{HNO}_2+\text{OH}} c_{\text{OH}}) \leq 40 \text{ pptv}$$

- photolysis of $\text{HNO}_3 \text{ ads}$, or $(\text{NO}_2 * \text{H}_2\text{O}) \text{ ads } j_{\text{NO}_3^-}$ too slow

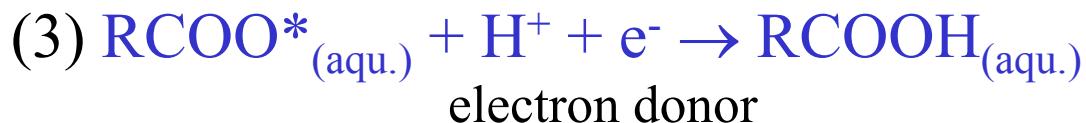
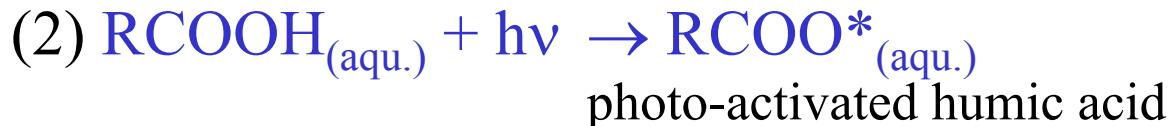
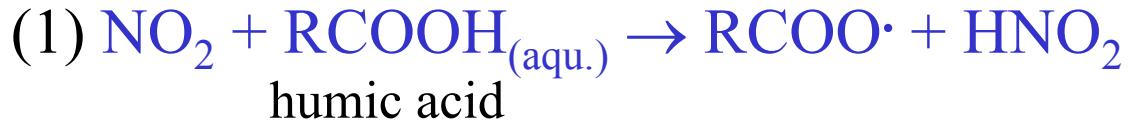
→ unexplained high day-time levels

(Staffelbach *et al.*, 1999; Akimoto *et al.*, 1987; Zhou *et al.*, 2003)

Day-time heterogeneous formation of nitrous acid

Photoinduced reaction: (?), $\sim j_{NO_2}$

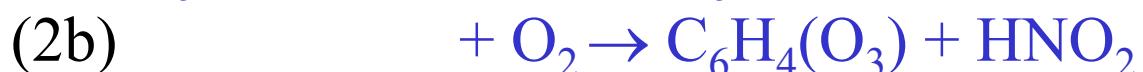
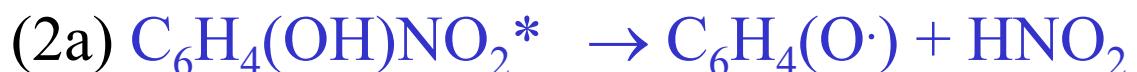
Photo-induced reduction:



(Kleffmann & Wiesen, 2005)

cannot explain lack of vertical gradient in at least 1 field measurement

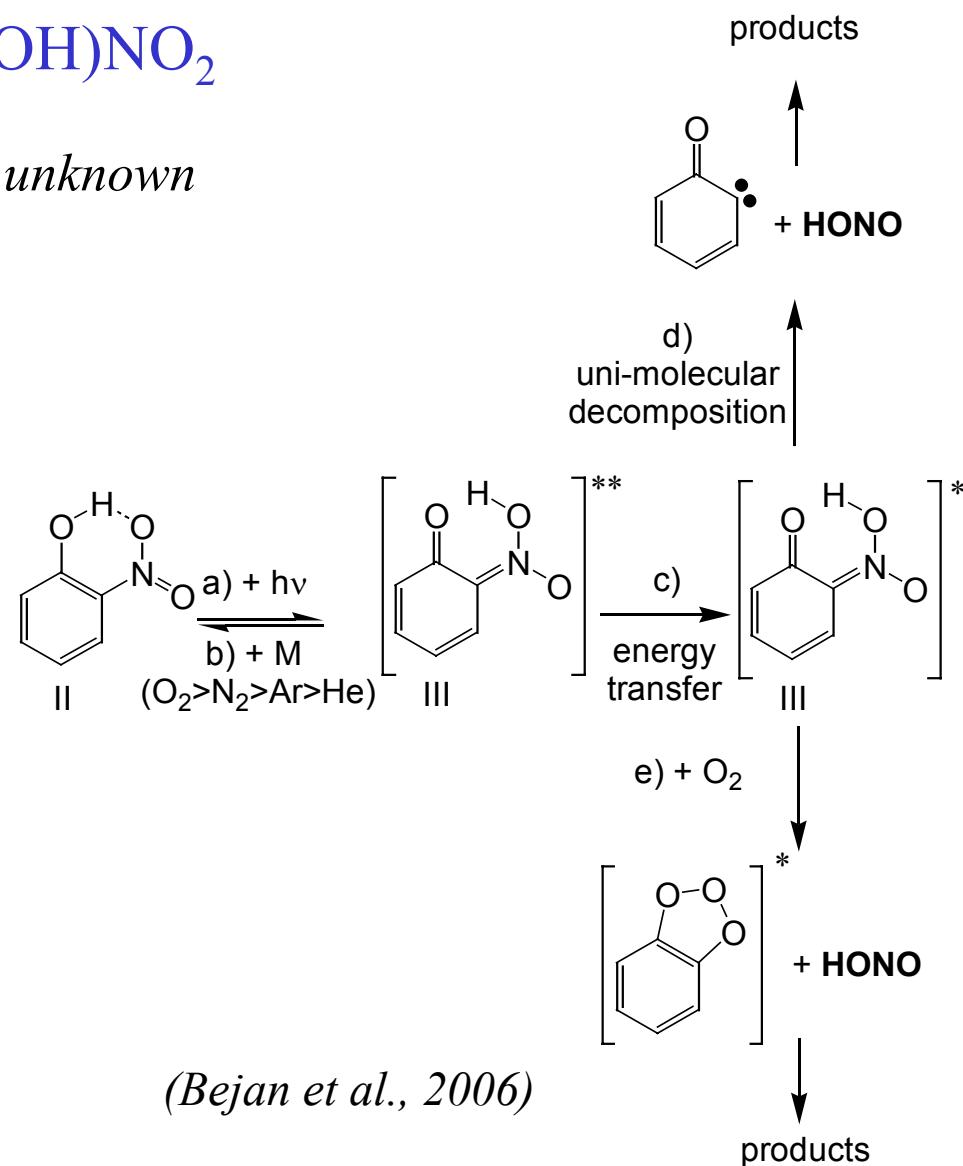
Photo-induced decomposition of nitro compound, i.e. nitrophenols:



Day-time heterogeneous formation of nitrous acid (2)

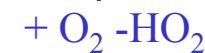
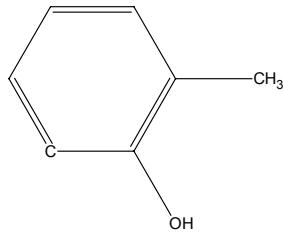
Photolysis of nitrophenols, $\phi(\text{OH})\text{NO}_2$

Significance in the atmosphere unknown

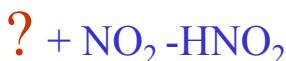


Degradation of monoaromatics: $\text{NO}_2 \rightarrow \text{HNO}_2$?

Example toluene:



(b)



(c)



Table 1. Rate constants, k_6 , for reactions of adducts, aromatic-OH, with O_2 and NO_2 and upper limits for the reactions with NO obtained by FP/RF at various temperatures (T in K), employing flash photolysis of H_2O ($> 160 \text{ nm}$) in 130 mbar of Ar.

$k (\text{cm}^3 \text{s}^{-1})$	Benzene ^a	Toluene ^a	m-Xylene ^c	p-Xylene	Hexamethylbenzene ^d	Aniline	Phenol ^a	m-Cresol
$k_{\text{O}_2}^{\text{add}} / 10^{-16}$	$1.6 \pm 0.6^b (299)$	$5.6 \pm 1.5^b (299)$	$18 \pm 5 (303)$	$8.8 \pm 2.5 (298)$		$6 \pm 2 (320)$	$300 \pm 70 (323)$	$640 \pm 150 (317)$
	$2.1 \pm 0.4^b (314)$	$5.6 \pm 0.6^b (321)$	$16 \pm 3 (323)$	$8.3 \pm 2.0 (308)$			$260 \pm 60 (333)$	$750 \pm 150 (319)$
	$3.0 \pm 0.3^b (333)$	$5.6 \pm 0.6 (339)$		$8.7 \pm 1.5 (319)$			$270 \pm 50^e (337)$	$> 800 (324)$
		$5.3 \pm 0.7 (347)$		$7.1 \pm 1.0 (327)$		$15 \pm 5 (340)$	$290 \pm 60 (343)$	$820 \pm 100 (334)$
	$3.7 \pm 0.4^b (354)$	$5.9 \pm 0.8 (354)$		$8.8 \pm 1.5 (332)$	$1800 \pm 300 (355)$	$9.6 \pm 3 (350)$	$270 \pm 60 (353)$	$800 \pm 100 (350)$
					$1200 \pm 200 (385)$		$360 \pm 50^e (363)$	
$k_{\text{NO}_2}^{\text{add}} / 10^{-11}$	$2.75 \pm 0.4 (305)$	$3.6 \pm 0.5 (300)$		$3.5 \pm 0.5 (317)$				$4 \pm 1 (317)$
	$2.45 \pm 0.3 (320)$	$3.6 \pm 0.4 (311)$						$4 \pm 1 (325)$
	$2.5 \pm 0.4 (333)$	$3.6 \pm 0.4 (320)$		$2.9 \pm 0.5 (330)$		$5 \pm 2 (330)$	$3.4 \pm 0.6^b (331)$	
	$2.5 \pm 0.4 (349)$	$4.0 \pm 0.6 (338)$					$4.1 \pm 0.7^b (354)$	
			$\text{c}_{\text{O}_2}/\text{c}_{\text{NO}_2} = 10^{-8}-10^{-6} > k_{\text{NO}_2}/k_{\text{O}_2}$					<i>(Koch et al., 2007)</i>
			$\rightarrow (\text{c}) \text{ does not occur}$					

2.2.5 Overview

