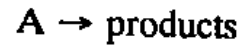


CHEMICAL KINETICS

FIRST-ORDER REACTIONS



rate constant k_1

The instantaneous reaction rate of compound A is given by

$$-d[A]/dt = k_1[A]$$

and depends only on the concentration of A. Hence,

$$-d[A]/[A]dt = -d \ln[A]/dt = k_1$$

and

$$\int -d \ln[A]/[A] = \int k_1 dt$$

Hence

$$\ln([A]_{t_0}/[A]_t) = k_1(t-t_0)$$

and

$$[A]_t = [A]_{t_0} e^{-k_1(t-t_0)}$$

The time for the initial concentration of A to decrease by 50%, i.e., $[A]_{t_0}/[A]_t = 2$, is the half-life, $\tau_{1/2}$, which is given by

$$\ln([A]_{t_0}/[A]_t) = \ln(2) = 0.6931 = k_1(\tau_{1/2})$$

and

$$\tau_{1/2} = 0.6931/k_1 = 0.6931(k_1)^{-1}$$

In this course, the lifetime, or τ , will be used, which is the time for the initial concentration to decrease to a value of $[A]_t/e = 0.368[A]_{t_0}$. Hence

$$\ln([A]_{t_0}/[A]_t) = \ln(e) = 1.000 = k_1\tau$$

and

$$\tau = 1/k_1 = k_1^{-1}$$

SECOND-ORDER REACTIONS



The instantaneous reaction rate and rate of formation of the products is given by

$$-d[A]/dt = -d[B]/dt = d[\text{products}]/dt = k_2[A][B]$$

Hence the instantaneous reaction rate and rate of formation of products is dependent on the concentration of compound A times that of compound B. If the concentration of A or B remains constant, or if one is in constant excess, then

$$-d[A]/dt = k'[A]$$

where $k' = k_2[B]$ (or $-d[B]/dt = k'[B]$ where $k' = k_2[A]$), and the reaction looks like a first-order reaction.

In this course, the concentration of one of the reactants, A or B, is assumed to be constant or an average 12-hr or 24-hr concentration is used. This allows the reaction to be treated as a pseudo-first order reaction, with

$$-d[A]/dt = k'[A]$$

where $k' = k_2[B]$. Then, after rearrangement and integration

$$\ln([A]_t/[A]_{t_0}) = k_2[B](t-t_0)$$

and

$$[A]_t = [A]_{t_0} e^{-k_2[B](t-t_0)}$$

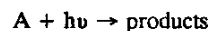
The lifetime of A is given by

$$\tau = 1/k_2[B] = (k_2[B])^{-1}$$

Note that the half-life is related to the lifetime by

$$\tau_{1/2} = 0.6931 \tau$$

Photolysis is in effect a second-order reaction



and the instantaneous rate of photolysis is

$$\text{photolysis rate} = -d[A]/dt = k_{\text{phot}}[A]$$

where the photolysis "rate constant" k_{phot} depends on the radiation flux (or light intensity) J , the absorption cross-section of the molecule, and the photolysis quantum yield for the wavelength interval involved. (This will be dealt with later in the course).

REACTIONS INVOLVING A THIRD-BODY, M

In atmospheric chemistry, several reactions involve a "third-body," M, and these involve the addition of species A to species B to yield the compound AB. The third-body, M, is required to remove the excess energy of reaction and allow the product AB species to be thermally stabilized.



In the atmosphere, M is air, which has a constant concentration at a given altitude. Hence these reactions reduce to a pseudo-second order reaction with an effective second-order rate constant

$$k' = k_3[M]$$

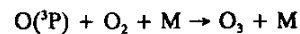
and

$$-d[A]/dt = -d[B]/dt = k'[A][B]$$

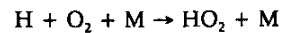
As is the case for second-order reactions, in this course one of the species A or B is assumed to have a constant or averaged concentration, and the lifetime of A is given by

$$\tau = (k_3[M][B])^{-1}$$

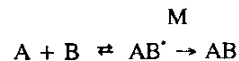
The two examples of third-order reactions which will be encountered in this class are



and



These third-order reactions are complex and involve three elementary reactions



CALCULATION OF LIFETIMES

For chemical compounds which are removed from the atmosphere by more than one process (for example, by both physical and chemical pathways), the overall lifetime, τ_{overall} , is given by

$$\tau_{\text{overall}} = (k_{\text{overall}})^{-1}$$

where k_{overall} is the removal rate (in time^{-1} units) of the chemical due to the various individual removal processes. For individual removal processes (1), (2), (3), etc., with removal rates of k_1, k_2, k_3 , etc., then

$$k_{\text{overall}} = k_1 + k_2 + k_3 + \dots$$

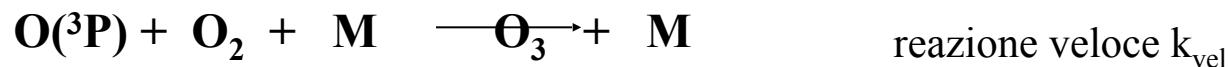
where k_1, k_2, k_3 , etc., include the concentrations of reactant(s) if they are second- or third-order reactions. Since

$$\tau_i = (k_i)^{-1}$$

then

$$(\tau_{\text{overall}})^{-1} = (\tau_1)^{-1} + (\tau_2)^{-1} + (\tau_3)^{-1} \text{ etc}$$

The individual lifetimes τ_1, τ_2, τ_3 , etc., are calculated as has been shown above.



dove j è la costante di fotolisi di NO_2 e k la costante di velocità per l'ultima reazione.

Poiché **quest'ultima reazione è veloce**, la concentrazione di O_3 nelle atmosfere urbane non può aumentare fino a che gran parte dello NO non è convertito a NO_2 .

Ciò spiega in parte il fatto che i livelli di O_3 siano inferiori nei centri urbani, dove avvengono notevoli emissioni di NO , che in aree suburbane sotto vento, dove NO_2 è trasportato e quindi fotodissociato con conseguente formazione di ozono. Tutte e tre le reazioni consecutive conducono a uno stato fotostazionario di ozono, la cui concentrazione è regolata dall'equazione:

$$[\text{O}_3] = \frac{J [\text{NO}_2]}{k [\text{NO}]}$$

La concentrazione dell'ozono nella troposfera è regolata **da uno stato stazionario che risulta dall'equilibrio dinamico tra produzione e distruzione e questa condizione non è una condizione di equilibrio**. Normalmente questa condizione, anche se impropriamente, viene chiamata **Equilibrio fotostazionario**.

Es. Calcoliamo la concentrazione la $[O_3]$ all'equilibrio fotostazionario.

Tipicamente in zona remota il rapporto $[NO_2]/[NO] = 1$

$$k = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecole}^{-1} \text{ s}^{-1}$$

Come abbiamo visto il tempo di vita di NO_2 è 1,7 minuti cioè 102 sec.

Ora ricordiamo che il tempo di emi-vita $\tau_{1/2}$ è il tempo in cui l'iniziale concentrazione decresce fino a metà, per cui in una equazione di 1 ordine o di pseudo-primo ordine si ottiene:

$$\ln([A]_{t_0}/[A]_t) = \ln(2) = 0.6931 = k_1(\tau_{1/2})$$

$$\tau_{1/2} = 0.6931/k_1 = 0.6931(k_1)^{-1}$$

$$\ln([A]_{t_0}/[A]_t) = \ln(e) = 1.000 = k_1\tau$$

$$\tau = 1/k_1 = k_1^{-1}$$

il tempo di vita τ è il tempo in cui l'iniziale concentrazione decresce fino al valore $[S]_{t_0}/e = 0.368$

$[S]_{t_0}$, ovvero significa che $[S]_t = [S]_{t_0}/e$

Per cui possiamo calcolare j.

$$J = 1/\tau = 1/102 \text{ s} = 0.01 \text{ s}^{-1}$$

Possiamo calcolare la $[O_3] = J [NO_2]/[NO] k = 5.5 \times 10^{11} \text{ molecole cm}^3$

STUDI CINETICI

Per studiare la cinetica e il meccanismo di una reazione bimolecolare è necessario seguire la concentrazione di uno o più tra reagenti e prodotti in funzione del tempo.

L'importanza di ottenere delle misure non soggette ad errori ha portato il gruppo di Riverside a sviluppare un metodo di misura relativa delle costanti cinetiche. Secondo questo metodo si introducono nella camera di reazione due composti organici che reagiscono entrambi con il radicale OH• (o il radicale NO₃•) [38]. Uno è il composto di cui si vuole determinare la costante di velocità (TEST), l'altro è un composto di riferimento (REF) scelto opportunamente e tale che la sua costante di velocità, nota, sia dello stesso ordine di grandezza della costante di velocità del test (in questo modo il tempo di decadimento del test è simile a quello del composto di riferimento)

Le reazioni competitive sono:



Il radicale OH• (NO₃•) deve essere introdotto in eccesso affinché le due reazioni del secondo ordine diventino reazioni dello pseudoprimo ordine per calcolare più agevolmente k_1 . Se $[\text{TEST}]_0$ e $[\text{REF}]_0$ sono le concentrazioni iniziali dei due reagenti e $[\text{TEST}]_i$ e $[\text{REF}]_i$ le concentrazioni dopo un certo tempo di reazione i , si può facilmente ricavare la seguente relazione:

$$\ln [\text{TEST}]_0 / [\text{TEST}]_i = k_1 / k_2 \ln [\text{REF}]_0 / [\text{REF}]_i \quad (3.10)$$

dove:

$$Y = \ln [\text{TEST}]_0 / [\text{TEST}]_i$$

$$X = \ln [\text{REF}]_0 / [\text{REF}]_i$$

$$Y = mX$$

ottenendo così una retta con coefficiente angolare $m = k_1 / k_2$

E' quindi sufficiente misurare le concentrazioni relative $[\text{TEST}]_0 / [\text{TEST}]_i$

e $[\text{REF}]_0 / [\text{REF}]_i$ a tempi diversi per ricavare immediatamente il rapporto tra le due costanti cinetiche e, sostituendo k_2 nota, si ottiene la costante incognita.

La tecnica delle cinetiche relative, oltre ad avere il grande vantaggio di non essere affetta da errori di calibrazione nella misura delle concentrazioni assolute, non richiede neppure la conoscenza esatta del tempo nel quale viene seguito il campionamento. Questo metodo permette inoltre di misurare direttamente le concentrazioni delle specie organiche anziché quella dell'intermedio radicalico. Ovviamente l'accuratezza delle costanti così calcolate dipende dall'accuratezza con cui è nota la costante delle specie di riferimento.

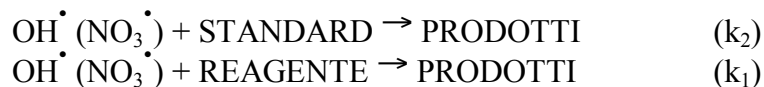
SCELTA DELLO STANDARD DI RIFERIMENTO

Per quanto riguarda la scelta dello standard, oltre alla caratteristica di non avere bande che si sovrappongono con quelle dei reagenti e dei composti che sono coinvolti per la formazione del radicale nitrato e del radicale ossidrilico, esso *deve avere costante di velocità dello stesso ordine di grandezza* del substrato indagato. Se così non fosse avremmo un consumo di radicale nitrato e del radicale ossidrilico dovuto solo ad uno dei due composti organici, impedendoci di valutare l'effettiva costante di velocità. Deve inoltre presentare *una legge cinetica dello stesso ordine* del nostro substrato.

DETERMINAZIONE DELLE COSTANTI DI VELOCITA'

METODO DELLE MISURE CINETICHE RELATIVE

* Utilizzato per la prima volta dal gruppo Atkinson a Riverside (CA, USA)
R. Atkinson, *J. Phys. Chem.*, **1991**, Vol.20, pp. 459.



$\text{OH}^\bullet (\text{NO}_3^\bullet)$ in eccesso per avere una reazione
dello PSEUDOPRIMORDINE

$$\ln [\text{STD}]_0 / [\text{STD}]_t = k_1 / k_2 \ln [\text{REA}]_0 / [\text{REA}]_t$$

$$\text{se } \ln [\text{STD}]_0 / [\text{STD}]_t = Y \quad \text{e} \quad \ln [\text{REA}]_0 / [\text{REA}]_t = X$$

$$Y = mX \quad m = k_1 / k_2 \quad k_2 \text{ nota in letteratura}$$

$$k_1 = m k_2$$

SCELTA DELLA BANDA

- L'intensità della banda deve essere compresa nell'intervallo di linearità dello strumento
- Deve essere in una regione spettrale in cui non cadono bande di assorbimento IR dei reagenti e di eventuali prodotti.

SCELTA DELLO STANDARD

- Deve seguire la stessa legge cinetica del reagente
- Deve avere costante di velocità dello stesso ordine di grandezza del substrato

DETERMINAZIONE DELLA COSTANTE DI VELOCITA'



Per lo Standard

$$-d[\text{STD}]/dt = k_1[\text{STD}] \quad -d[\text{STD}]/[\text{STD}] = k_1 dt$$

$$\ln[\text{STD}] = -k_1 t + C$$

$$t = 0 \rightarrow [\text{STD}]_0 \quad \ln[\text{STD}] = \ln[\text{STD}]_0 - k_1 t$$

$$1) \quad \ln[\text{STD}]/[\text{STD}]_0 = -k_1 t$$

Per il Reagente

$$-d[\text{REA}]/dt = k_2[\text{REA}] \quad -d[\text{REA}]/[\text{REA}] = k_2 dt$$

$$\ln[\text{REA}] = -k_2 t + C$$

$$t = 0 \rightarrow [\text{REA}]_0 \quad \ln[\text{REA}] = \ln[\text{REA}]_0 - k_2 t$$

$$2) \quad \ln[\text{REA}]/[\text{REA}]_0 = -k_2 t$$

Se uguagliamo **1 = 2**

$$1/k_2 \ln[\text{REA}]/[\text{REA}]_0 = 1/k_1 \ln[\text{STD}]/[\text{STD}]_0$$

$$\ln[\text{STD}]/[\text{STD}]_0 = k_1/k_2 \ln[\text{REA}]/[\text{REA}]_0$$

CONDIZIONI:

$$[\text{O}_3] = 34 \text{ ppm} = 10,40 * 10^{-2} \text{ mmoli}$$

$$[\text{NO}_2] = 100 \text{ ppm} = 3200 * 10^{-4} \text{ mmoli}$$

$$[\text{REA}] = 11 \text{ ppm} = 1,200 * 10^{-2} \text{ mmoli}$$

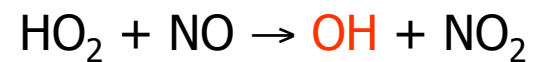
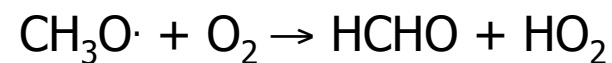
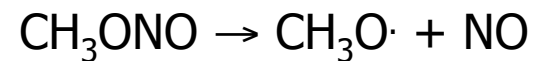
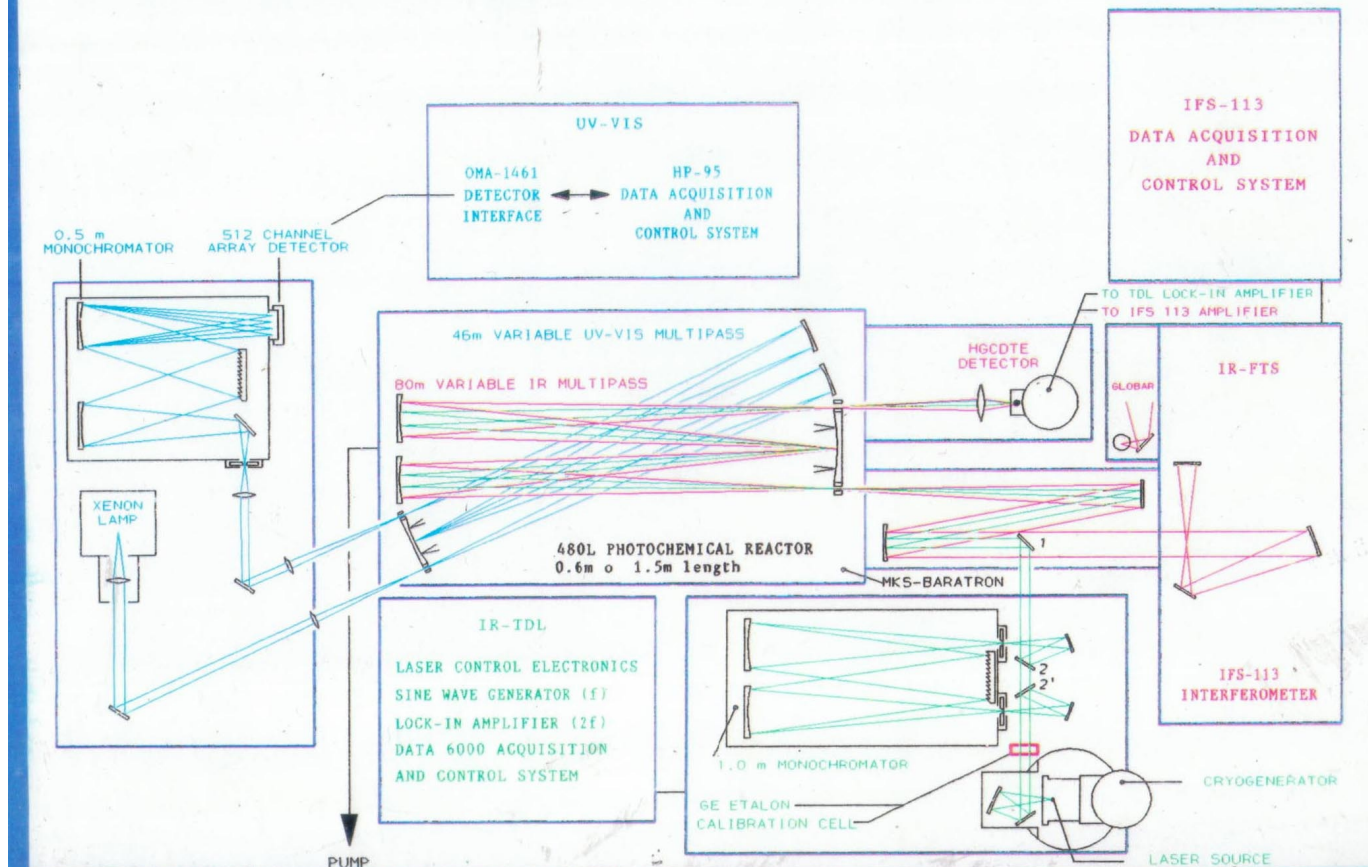
COSTANTI DI VELOCITA'

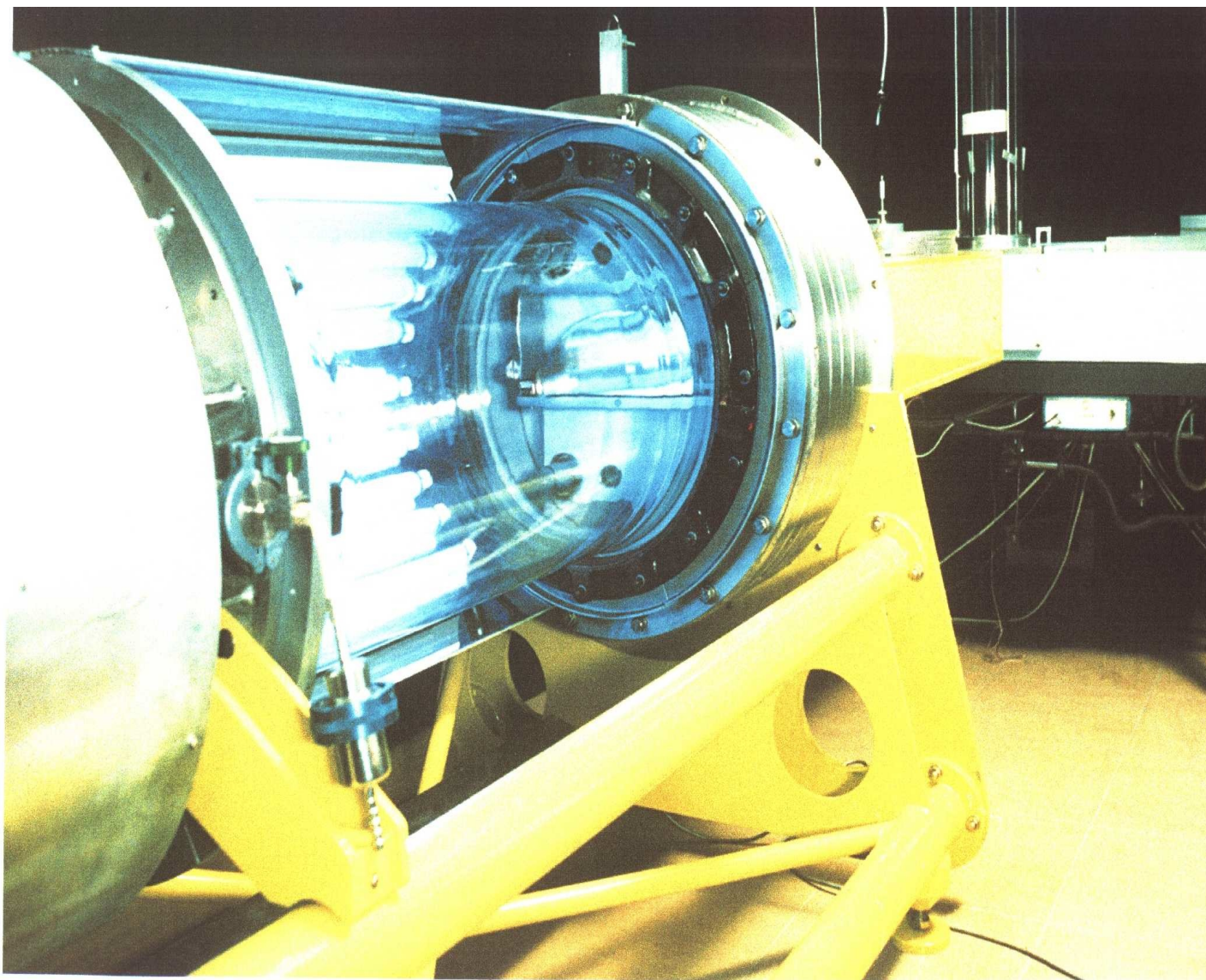
- TRE ESPERIMENTI PER OGNI REAZIONE

- UNO O DUE STANDARD INTERNI PER OGNI REAGENTE

<i>SUBSTRATO</i>	<i>STANDARD</i>	<i>k (NO₃[•]) (cm³ molecole⁻¹ s⁻¹)</i>
p-Metossitoluene	1,3,5-trimetilbenzene	3.12 ± 0.54 10 ⁻¹⁵
	4-metiltoluene	2.16 ± 0.40 10 ⁻¹⁵
p-Etossitoluene	1,3,5-trimetilbenzene	2.67 ± 0.53 10 ⁻¹⁵
	4-metiltoluene	2.00 ± 0.34 10 ⁻¹⁵
p-isopropiltoluene	4-metossibenzene	9.98 ± 0.15 10 ⁻¹⁶
p-Tertbutiltoluene	4-metossibenzene	5.99 ± 0.45 10 ⁻¹⁶
	etilene	7.15 ± 0.45 10 ⁻¹⁶
p-Etiltoluene	1,3,5-trimetilbenzene	7.71 ± 1.10 10 ⁻¹⁶
<i>SUBSTRATO</i>	<i>STANDARD</i>	<i>k (OH[•]) (cm³ molecole⁻¹ s⁻¹)</i>
p-isopropiltoluene	etilene	15.94 ± 1.30 10 ⁻¹²
p-tertbutiltoluene	etilene	13.96 ± 0.89 10 ⁻¹²

JRC-ISPRA • STUDIES OF ATMOSPHERIC CHEMISTRY
 REACTION CHAMBER INSTRUMENTED WITH ANALYTICAL SPECTROSCOPIC TECHNIQUES

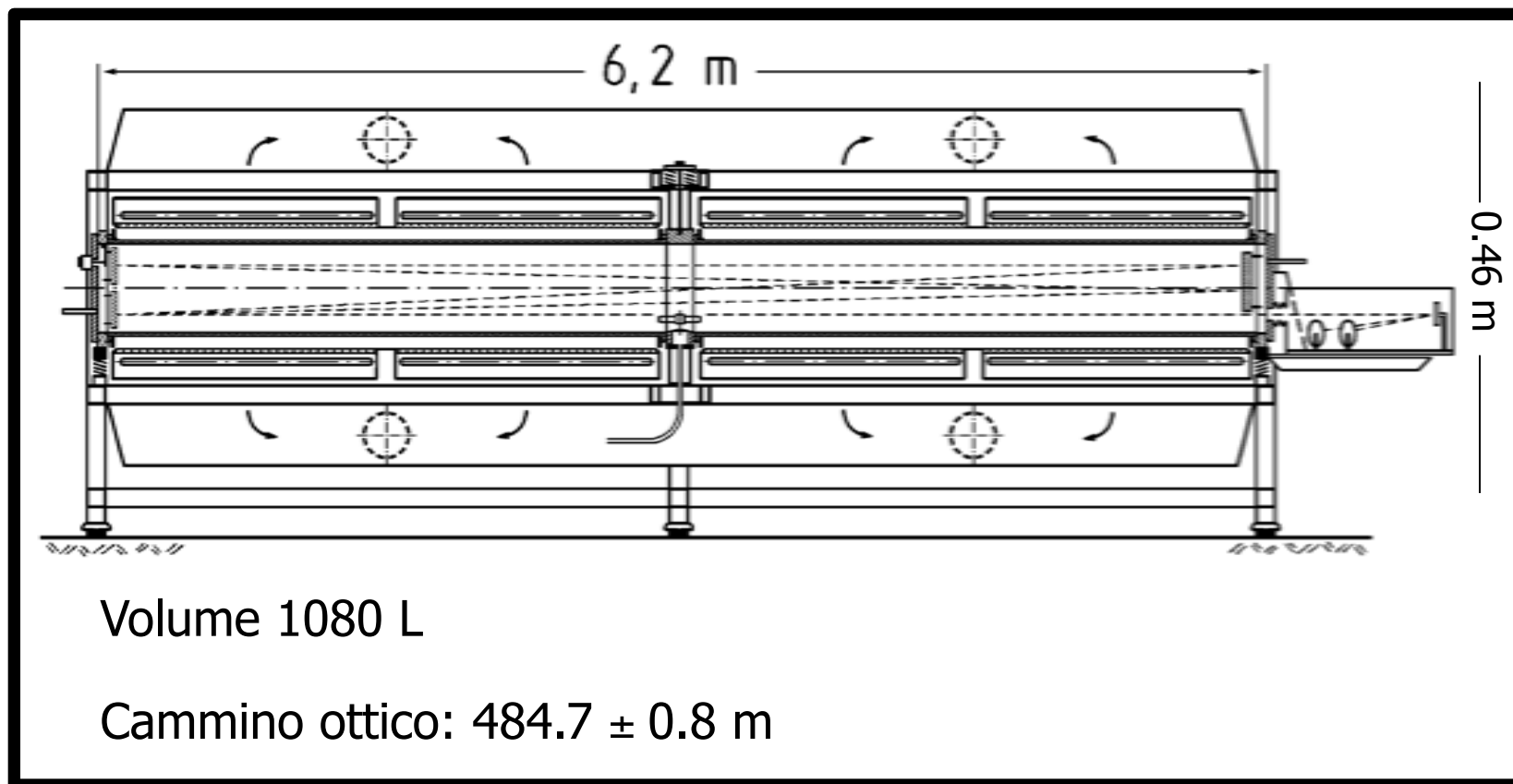




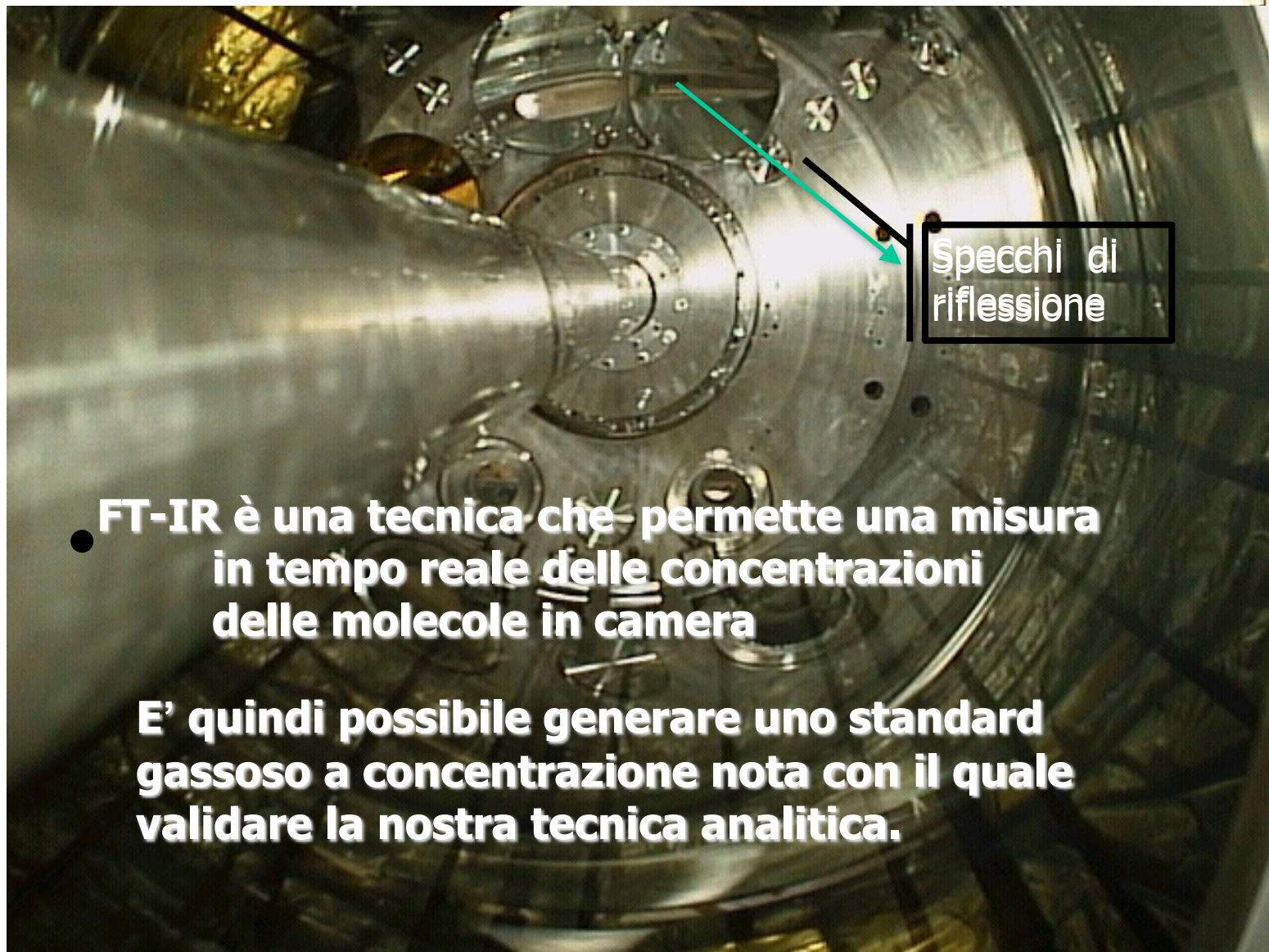
480 L Reaction chamber

SMOG-CHAMBER FI-IR DETECTOR

Dipartimento di Chimica-Fisica
dell'Università di Wuppertal



SMOG-CHAMBER FI-IR DETECTOR



Specchi di riflessione

- FT-IR è una tecnica che permette una misura in tempo reale delle concentrazioni delle molecole in camera

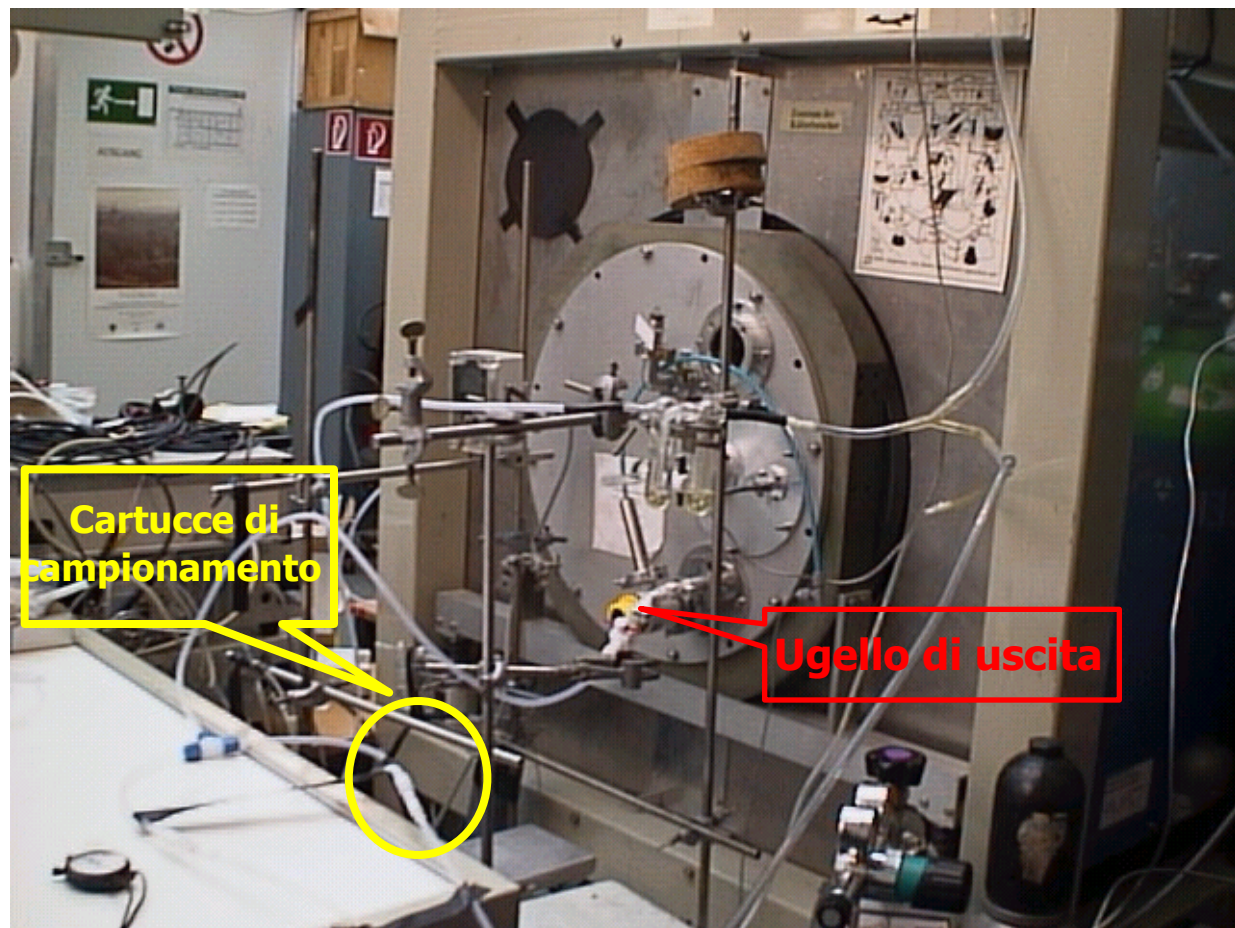
E' quindi possibile generare uno standard gassoso a concentrazione nota con il quale validare la nostra tecnica analitica.

CAMPIONAMENTO

- Introduzione dello standard in camera
- Campionamento per 20 min.
Flusso di 50 ml min.

INTERCALIBRAZIONE

- Analisi in HPLC-DAD
- Calcolo delle concentrazioni presenti in camera
- Confronto con quelle rilevate dall'FT-IR



Particolare del sistema di campionamento

Grandi quantità di VOC sono emessi in troposfera da fonti antropiche e biogeniche. Quelli di origine antropica derivano principalmente da processi di combustione incompleta o evaporazione, produzione di energia elettrica, agricoltura e processi industriali (es. solventi).

Il metano risulta essere il VOC più abbondante ed è immesso in atmosfera sia da fonti antropiche che biogeniche; si stima che le emissioni mondiali di origine biogenica siano pari a 155-240 milioni di tonnellate/anno mentre quelle di origine antropica si aggirerebbero intorno a 350-375 milioni di tonnellate/anno^[i].

Grandi quantità di composti organici non metanici (NMOC, Non Methanic Organic Compounds) sono emessi dalla vegetazione (isoprene, C₁₀H₁₆ monoterpeni, C₁₄H₂₄ sesquiterpeni, e VOC ossigenati). I NMOC sono emessi in troposfera anche da una serie di fonti antropiche. Alcune stime delle emissioni di **NMOC di origine antropica riportate in letteratura si aggirano intorno a 60-140 milioni di tonnellate/anno**, mentre il contributo di origine biogenica raggiungerebbe circa 1150 milioni di tonnellate/anno.^{[ii],[iii]}

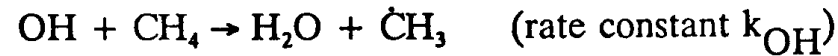
^[i] **Hein, R., Crutzen, P.J., Heimann, M., 1997.** An inverse modeling approach to investigate the global atmospheric methane cycle. *Global Biogeochemical Cycles* 11, 43-76.

^[ii] **Lamb, B., Gay, D., Westberg, H., Pierce, T., 1993.** A biogenic hydrocarbons emission inventory for the, U.S.A. using a simple forest canopy model. *Atmospheric Environment*, 27A, 1673-1690.

^[iii] **Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., Zimmermann, P., 1995.** A global model of natural volatile organic compound emissions. *Journal of Geophysical Research* 100, 8873-8892.

Reaction with the OH Radical

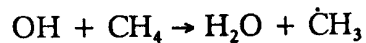
Methane reacts with the OH radical, and this reaction is the sole chemical removal process for methane in the troposphere.



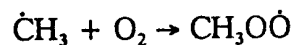
The only other tropospheric removal process for methane is upward transport from the troposphere to the stratosphere and subsequent reaction in the stratosphere (again with the OH radical). Because of the slow vertical mixing in the stratosphere and the lower methane concentration at the tropopause (due to the lower total pressure at the tropopause, since the CH_4 mixing ratio is constant throughout the troposphere), transport from the troposphere to the stratosphere is relatively minor.

METHANE OXIDATION CYCLE IN THE PRESENCE OF NO_x

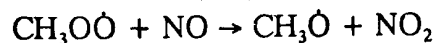
The initial reaction leads to the formation of the methyl ($\dot{\text{C}}\text{H}_3$) radical.



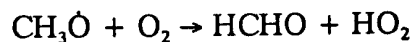
In the troposphere, the only reaction of the methyl radical is to add O₂ to form the methyl peroxy ($\text{CH}_3\text{O}\dot{\text{O}}$) radical. The lifetime of the $\dot{\text{C}}\text{H}_3$ radical is $\sim 10^{-6}$ s.



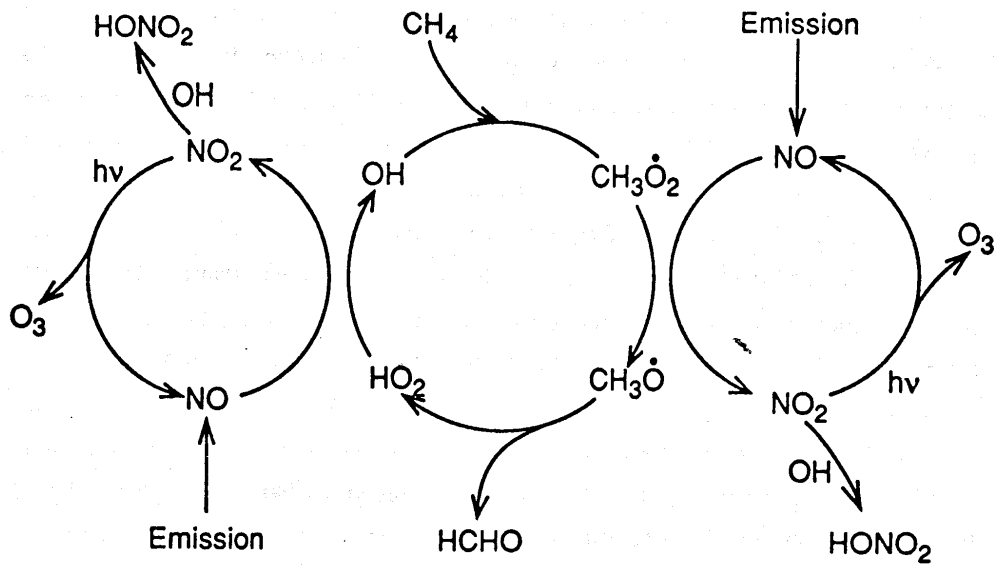
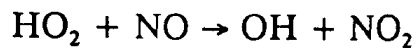
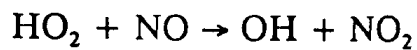
In the presence of sufficient NO, the methyl peroxy radical reacts with NO to generate the methoxy ($\text{CH}_3\dot{\text{O}}$) radical and NO₂.



In the troposphere, the only important reaction of the methoxy radical is with O₂ to form formaldehyde (HCHO) and the hydroperoxyl (HO₂) radical. The lifetime of the $\text{CH}_3\dot{\text{O}}$ radical in the lower troposphere is $\sim 10^{-4}$ s.

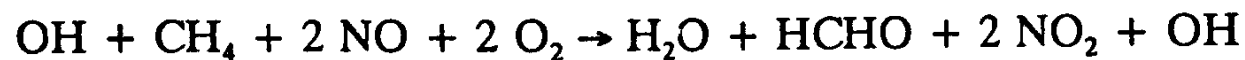


In the presence of sufficient NO, the HO₂ radical reacts with NO to regenerate the OH radical



Reaction scheme for the oxidation of CH₄ to HCHO in the presence of NO

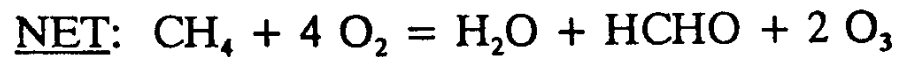
In the presence of NO, the oxidation of CH₄ to HCHO leads to the oxidation of NO to NO₂ and the formation of ozone in the troposphere, with:



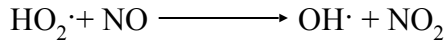
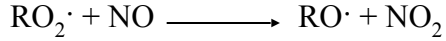
Since



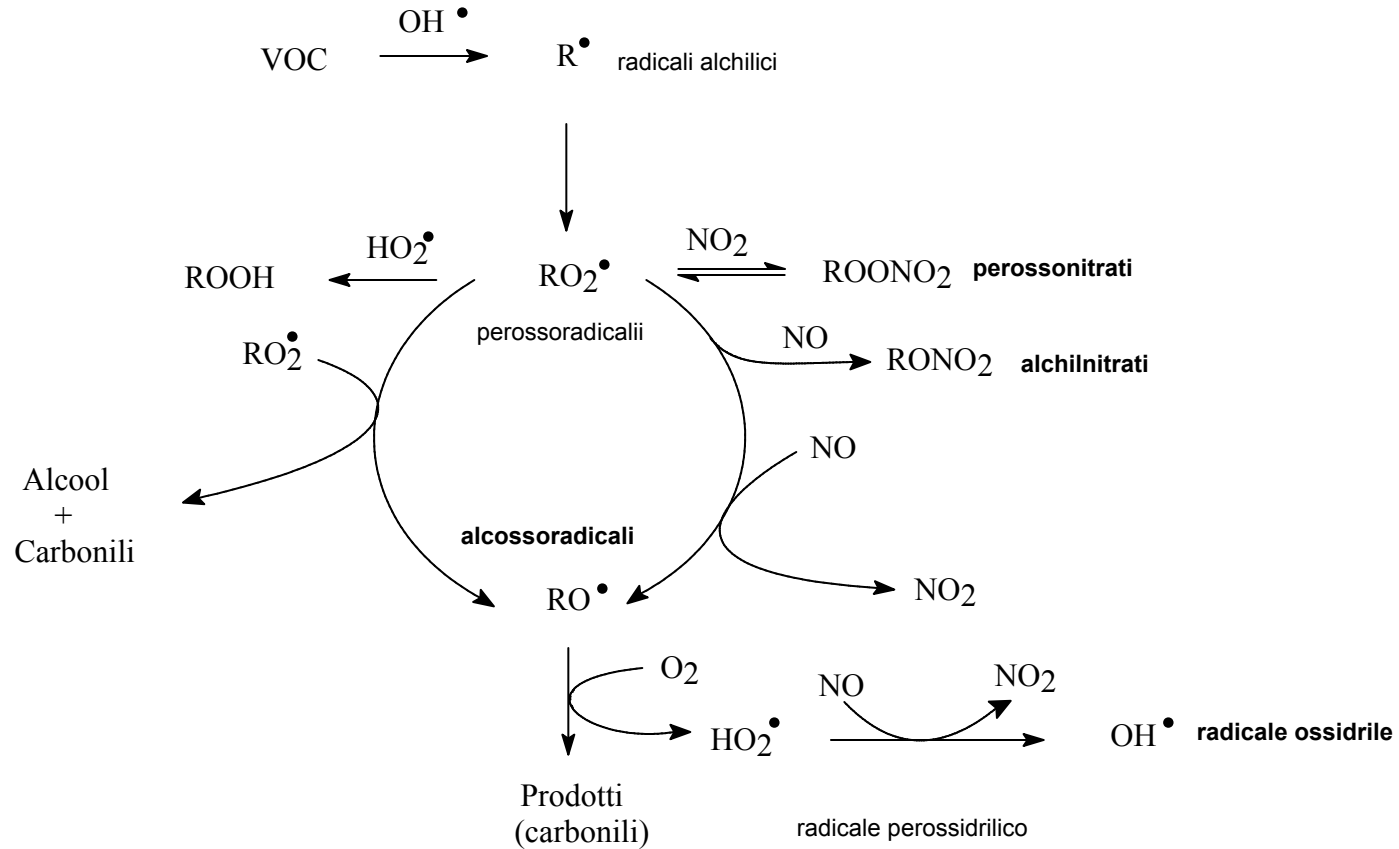
then



La presenza in troposfera di VOC che subiscono processi di fotossidazione (con un attacco iniziale essenzialmente legato al radicale ossidrilico, OH·) porta alla formazione di perossiradicali HO₂· e RO₂·; questi competono efficacemente con l'ozono nel riossidare l'NO a NO₂ (la minor concentrazione è compensata da valori più elevati delle costanti di velocità di reazione):



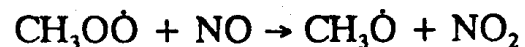
che viene poi fotolizzato a formare O₃. Come è evidenziato questo processo di fatto rompe l'equilibrio fotostazionario permettendo l'accumulo di O₃.



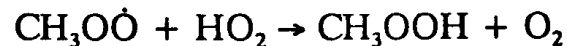
OXIDATION OF METHANE AT LOW TROPOSPHERIC NO CONCENTRATIONS

However, clean tropospheric NO mixing ratios are generally low, being ~5-30 ppt in the lower troposphere and ~50-100 ppt in the upper troposphere.

In the methane oxidation cycle, there are two reactions which involve the competition of NO with peroxy radicals. These are:



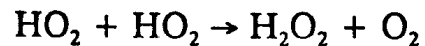
in competition with



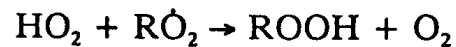
HO₂



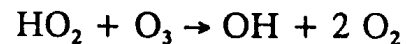
in competition with



and

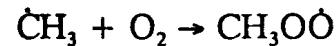
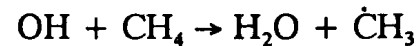


and

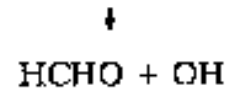
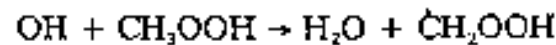
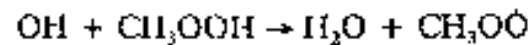
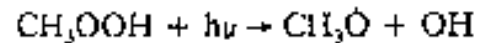


Based on the estimated concentrations of HO₂ and other organic peroxy (RO₂) radicals, the O₃ concentrations, and the rate constants for these reactions, the reactions of HO₂ and CH₃O[•] radicals with NO dominate for NO concentrations $\geq (3-7) \times 10^8$ molecule cm⁻³ in the lower troposphere ($\geq 10-30$ ppt).

For low-NO concentration conditions, the oxidation of methane proceeds by:

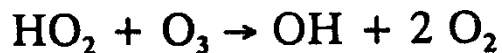


where CH_3OOH is methyl hydroperoxide. CH_3OOH photolyzes and reacts with the OH radical at similar rates in the troposphere (overall lifetime of CH_3OOH is ~2 days).



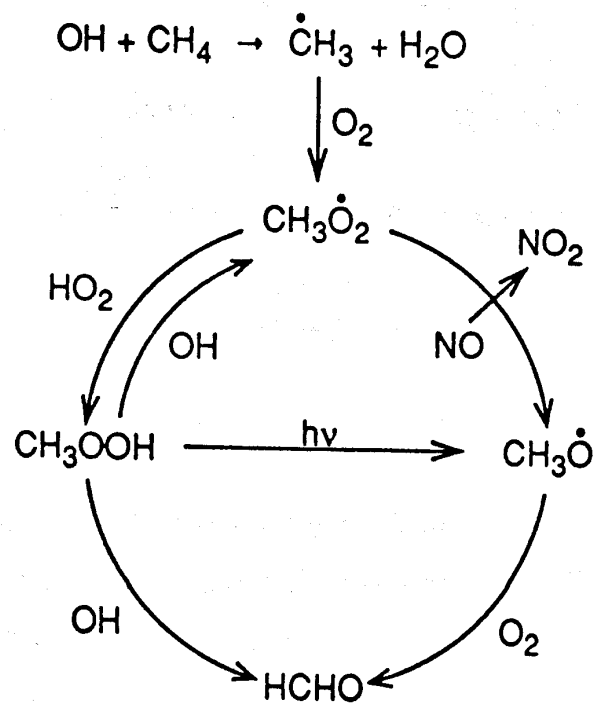
The final product is still HCHO (although CH_3OOH can be removed from the troposphere by rain-out (wet deposition) and dry deposition), but NO is not converted to NO_2 and O_3 is not produced.

In fact, in the absence of NO, or for NO mixing ratios ≤ 30 ppt, methane oxidation acts as a "sink" for HO_x (OH + HO₂), and leads to the destruction of ozone, in part through the reaction



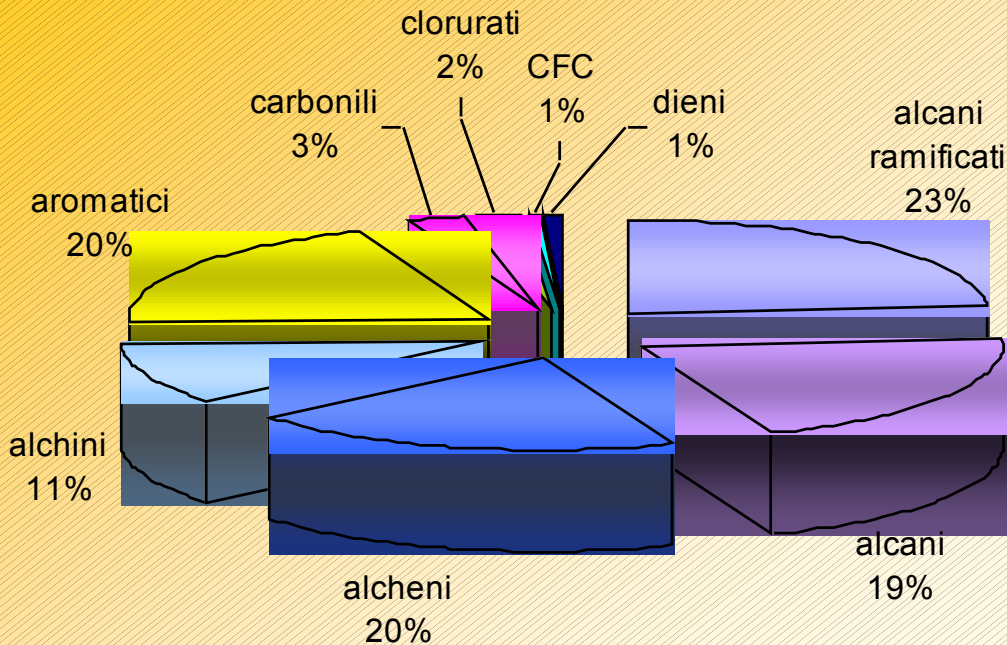
and also because the initial formation of the OH radical involves the photolysis of O₃ (so any lack of O₃ formation is an overall loss process).

A schematic of the methane oxidation cycle is shown below:



It is believed that the oxidation of methane leads to the net destruction of O_3 in the clean lower troposphere over oceanic areas, and a net production of O_3 in the middle and upper troposphere, with these O_3 formation/loss rates approximately balancing in the troposphere as a whole.

VOC IN LOMBARDIA



➤ Alcani

→ Maggiori costituenti dei combustibili sia per riscaldamento che per veicoli (fino al 55-65%)

➤ Alcheni

→ Costituenti minori dei combustibili 5-10% e composti di origine industriale (es. etilene usato nella formazione dei polimeri)

➤ Alchini

→ Composti di origine industriale

➤ Aromatici

→ Costituenti delle benzine e utilizzati come solventi

➤ Carbonili

→ •emissioni dirette
•formazione per via fotochimica

➤ CFC e composti clorurati

→ Protocollo Montreal

Measurements of Ozone Precursors in Urban Areas and at Highways, Th. Schimitz, D. Klemp and D. Kley, Eurotrac Symposium '98.



COMPOSTI CAMPIONATI

LOCALITA' I CAMPIONAMENTO	etano	propano	butano	pentano	esano	eptano	ottano	nonano	decano	undecano
Valmasino	3,15	1,32	0,50	0,20	0,09	0,05	0,02	0,02	0,03	0,01
Iseo	4,15	3,86	1,19	0,35	0,14	0,08	0,51	0,03	0,09	0,09
Fiume Oglio	5,31	4,46	3,59	1,19	0,50	0,42	0,06	0,04	0,53	0,11
Sondrio	4,70	11,75	5,10	1,95	0,72	0,49	1,63	0,10	0,53	0,15
Lecco	33,34	10,80	21,23	16,76	5,59	4,68	2,35	0,45	2,56	0,52
Varenna	3,62	4,05	1,47	0,76	0,24	0,18	0,09	0,03	0,17	0,08
Bergamo	9,61	5,21	5,06	2,26	0,86	0,52	1,49	0,10	0,53	0,10
Bergamo (zona ind.)	12,64	7,41	9,29	3,47	1,21	1,83	0,79	0,17	0,70	0,19
Brescia	14,68	11,69	4,48	2,22	0,62	0,45	0,40	0,27	0,31	0,12
Milano	30,74	15,83	15,86	11,24	4,82	3,01	1,62	0,65	1,81	0,82
Milano 20 m	23,04	11,36	8,88	4,64	2,23	1,10	0,52	0,27	0,71	0,34
Bresso	34,61	15,70	14,03	17,25	3,72	2,89	0,16	0,38	1,13	0,52
Agrate (zona ind.)	25,57	12,65	9,60	8,12	1,87	1,00	0,99	0,20	0,68	0,23
Parabiago	39,99	19,71	13,99	9,34	3,92	2,88	1,07	0,35	1,40	0,40
Parabiago 20 m	36,03	15,38	9,81	5,15	2,80	1,79	0,18	0,28	0,75	0,33
Varese	14,80	5,52	8,47	5,41	1,85	1,63	0,69	0,24	1,03	0,30
Lurate Caccivio (ind.)	12,07	5,49	3,75	2,58	0,78	0,52	0,60	0,25	0,62	0,60
Como/CH	15,40	8,03	5,17	2,13	0,72	0,49	0,26	0,17	0,34	0,18
Cremona	33,17	15,18	28,50	11,50	6,21	5,89	2,53	0,64	5,06	0,43
Cremona (zona ind.)	64,96	30,03	52,14	12,83	5,18	4,62	2,17	0,60	4,23	0,48
Mantova	11,34	10,06	8,54	3,39	1,22	0,94	0,52	0,18	0,68	0,21
Mantova (zona ind.)	7,11	8,33	3,37	2,25	0,49	0,26	0,10	0,07	0,16	0,12
Lodi	46,24	90,62	72,66	16,91	8,85	5,61	2,44	0,51	3,57	0,32
Pavia	25,67	11,28	14,01	7,89	3,16	2,54	1,33	0,29	1,18	0,17
media	21,33	13,99	13,36	6,24	2,41	1,83	0,94	0,26	1,20	0,28

COMPOSTI CAMPIONATI

LOCALITA' I CAMPIONAMENTO	COMPOSTI CAMPIONATI													
	i-butano	2,3-dimetilbutano	2-metilpentano	3-metil-pentano	i-pentano	neo-pentano	2,3-dimetilpentano	2,4-dimetilpentano	2,3,4-trimetilpentano	2-metilesano	3-metilesano	2-metileptano	3-metileptano	i-ottano
Valmasino	0,44	0,03	0,19	0,09	0,56	0,22	0,00	0,06	0,00	0,06	0,13	0,02	0,08	0,04
Iseo	0,76	0,07	0,35	0,22	1,30	0,12	0,03	0,02	0,00	0,08	0,12	0,04	0,03	0,08
Fiume Oglio	2,19	0,45	1,61	0,98	5,84	0,60	0,14	0,09	0,06	0,44	0,51	0,12	0,17	0,28
Sondrio	3,14	0,97	2,75	1,57	9,57	0,97	0,24	0,16	0,15	0,62	0,73	0,16	0,19	0,59
Lecco	13,72	0,00	17,77	10,27	71,02	9,48	2,08	1,22	1,31	5,68	6,19	1,53	1,94	5,05
Varenna	0,94	0,12	0,59	0,34	2,60	0,30	0,06	0,02	0,04	0,21	0,25	0,08	0,06	0,12
Bergamo	3,19	0,86	2,90	1,76	10,69	0,95	0,26	0,18	0,15	0,73	0,78	0,20	0,26	0,63
Bergamo (zona ind.)	5,40	1,22	4,31	2,59	15,37	1,58	0,45	0,30	0,24	1,41	1,66	0,31	0,41	1,13
Brescia	3,09	0,34	1,38	0,90	5,30	0,55	0,14	0,12	0,06	0,36	0,45	0,12	0,15	0,31
Milano	9,51	4,60	13,17	8,01	44,87	5,90	1,62	1,00	1,24	3,95	4,31	1,21	1,45	4,59
Milano 20 m	5,85	1,63	5,27	3,15	17,86	1,98	0,47	0,33	0,39	1,49	1,58	0,36	0,42	1,53
Bresso	8,66	3,10	9,90	5,85	33,22	4,55	1,17	0,79	0,89	3,32	3,62	0,84	1,10	3,42
Agrate (zona ind.)	5,72	1,51	4,34	2,57	16,97	2,21	0,42	0,33	0,31	1,29	1,40	0,29	0,35	1,39
Parabiago	8,79	3,27	9,76	5,73	34,41	4,77	1,19	0,73	0,75	3,08	3,43	0,81	1,05	2,93
Parabiago 20 m	6,49	1,90	5,86	3,53	18,73	2,33	0,61	0,42	0,37	1,67	1,85	0,41	0,57	1,45
Varese	4,80	2,99	6,76	3,79	23,54	2,97	0,81	0,50	0,77	1,87	2,14	0,63	0,86	2,35
Lurate Caccivio (ind.)	1,96	0,77	1,89	1,09	7,98	0,95	0,19	0,15	0,14	0,59	0,66	0,17	0,19	0,53
Como/CH	3,44	0,90	2,08	1,27	8,67	1,18	0,24	0,16	0,21	0,60	0,68	0,15	0,20	0,82
Cremona	16,69	6,94	23,18	13,90	73,84	6,45	2,65	1,43	1,09	6,59	7,69	1,83	2,50	4,37
Cremona (zona ind.)	37,96	6,52	21,00	12,65	98,63	8,06	2,13	1,30	0,97	5,38	6,00	1,45	2,04	4,17
Mantova	5,17	1,19	4,24	2,62	15,31	1,60	0,47	0,40	0,23	1,08	1,25	0,33	0,41	1,00
Mantova (zona ind.)	2,16	0,21	0,87	0,56	3,59	0,37	0,07	0,04	0,03	0,22	0,29	0,04	0,08	0,17
Lodi	42,85	6,89	23,28	14,36	73,14	9,23	2,44	1,74	2,29	7,20	7,47	2,00	2,64	8,54
Pavia	9,62	3,93	14,48	9,15	44,54	4,69	1,59	1,10	1,42	3,77	3,94	1,07	1,37	5,39
media	8,44	2,10	7,41	4,46	26,57	3,00	0,81	0,53	0,55	2,15	2,38	0,59	0,77	2,12

Calculated Tropospheric Lifetimes of Selected Alkanes
Due to Reaction with OH Radicals, NO₃ Radicals and O₃

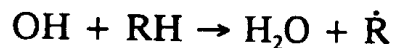
Alkane	Lifetime due to Reaction with ^a		
	OH	NO ₃	O ₃
Propane	12 days	7.5 yr	>4500 yr
n-Butane	5.7 days	3.4 yr	>4500 yr
2-Methylpropane	6.2 days	1.2 yr	>4500 yr
n-Hexane	2.6 days	1.3 yr	>4500 yr
n-Nonane	1.4 days	190 days	>4500 yr

^aUsing the concentrations of OH radicals, NO₃ radicals and O₃ given in the text.

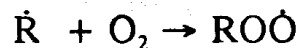
Clearly, reaction with the OH radical is the dominant tropospheric removal/transformation process for the alkanes.

Ethane has a tropospheric lifetime with respect to reaction with the OH radical of ~2 months, long enough for transport on a global scale. For urban airshed conditions, ethane is essentially non-reactive.

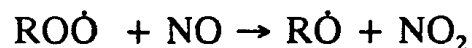
In urban areas, the concentrations of NO_x are generally sufficiently high that the dominant reactions of peroxy radicals [HO_2 and organic peroxy (ROO) radicals] are with NO . The simplest alkanes then react in a manner totally similar to methane. Denoting the alkane as RH (for methane, $\text{R} = \text{CH}_3$), then



where $\dot{\text{R}}$ is an alkyl radical,



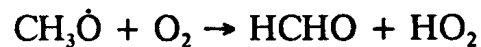
where ROO is an alkyl peroxy radical,



leading to the formation of the alkoxy (RO) radical.

So far, this sequence is totally analogous to that for the OH radical-initiated reaction of CH_4 to form the methoxy ($\text{CH}_3\dot{\text{O}}$) radical.

However, while the methoxy radical reacts only with O_2 to form formaldehyde,



the alkoxy radicals formed from the more complex alkanes can react with O_2 ,

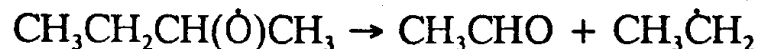


or decompose,



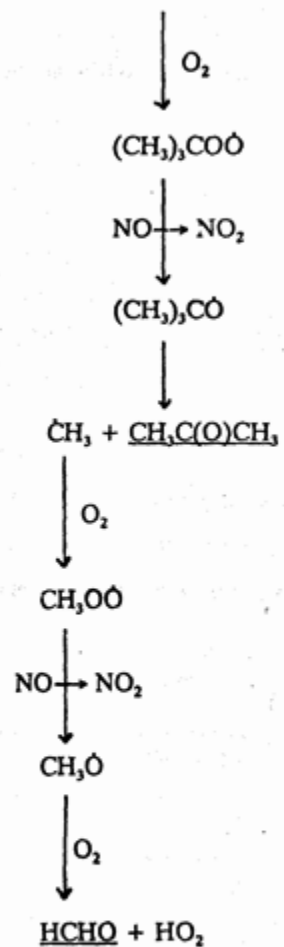
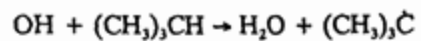
where $R_1\dot{}$ has less carbon atoms than has the alkoxy radical $R\dot{O}$.

For example, for the $CH_3CH_2CH(\dot{O})CH_3$ alkoxy radical formed from n-butane,

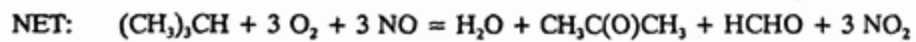
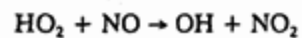


The alkyl radical $R_1\dot{}$ produced in the decomposition reaction then undergoes a series of reactions analogous to those shown above for the \dot{R} radical.

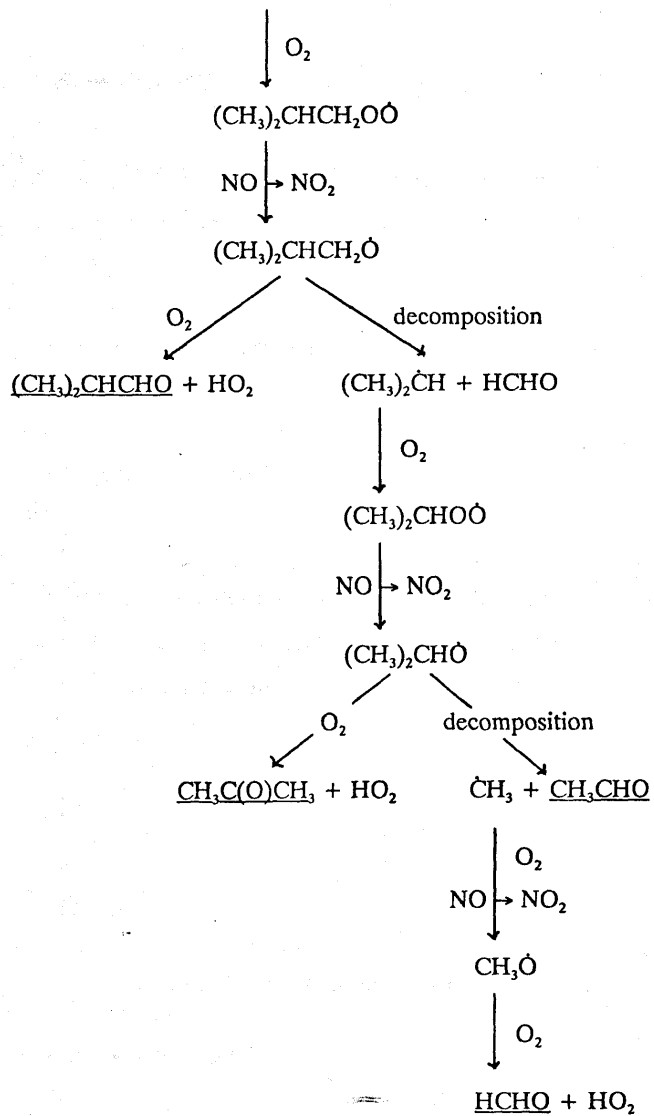
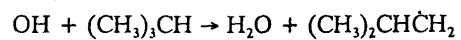
Abstraction of the tertiary H atom:



followed by regeneration of the OH radical.



Abstraction of a primary H atom:



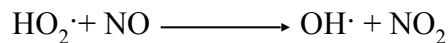
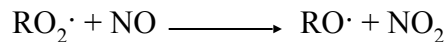
followed by regeneration of the OH radical.



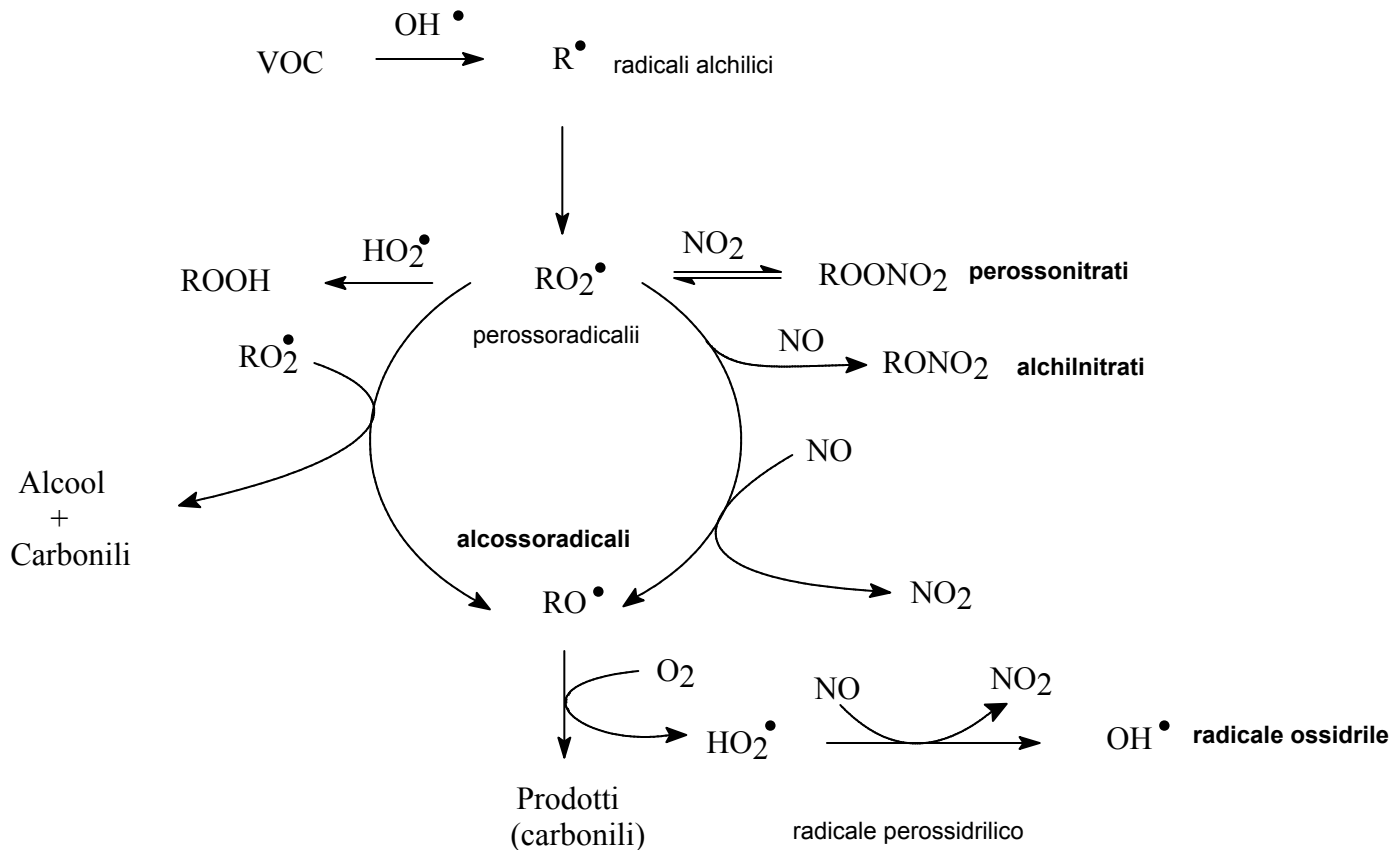
As for the methane oxidation cycle, the OH radical-initiated reactions of the alkanes in the presence of sufficient NO lead to the formation of carbonyl compounds and the conversion of NO to NO₂. The subsequent photolysis of NO₂ leads to the formation of O₃, and hence to photochemical air pollution).



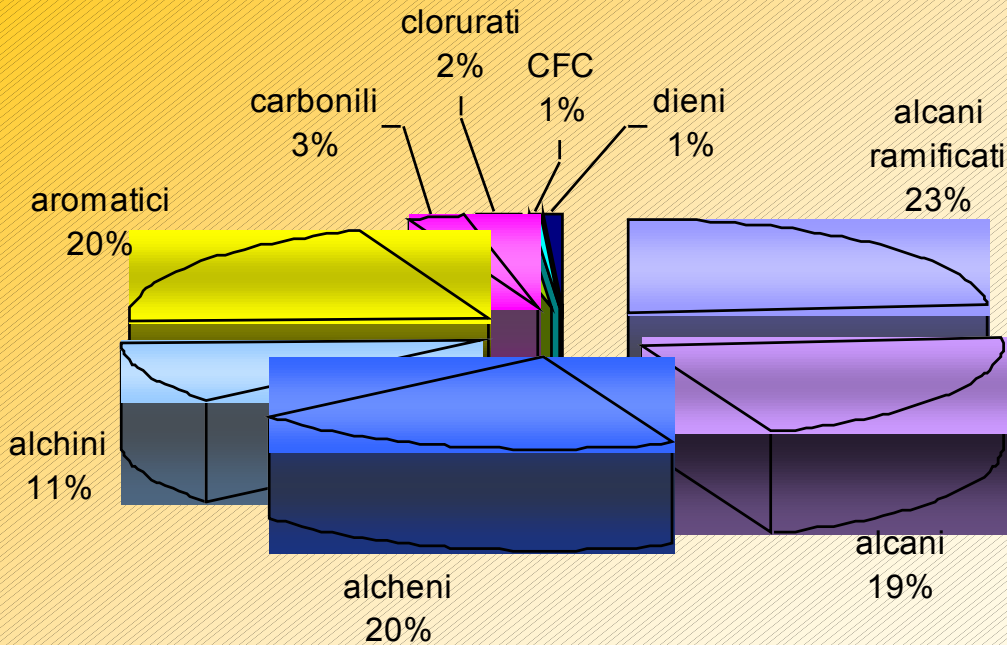
La presenza in troposfera di VOC che subiscono processi di fotossidazione (con un attacco iniziale essenzialmente legato al radicale ossidrilico, OH·) porta alla formazione di perossiradicali HO₂· e RO₂·; questi competono efficacemente con l'ozono nel riossidare l'NO a NO₂ (la minor concentrazione è compensata da valori più elevati delle costanti di velocità di reazione):



che viene poi fotolizzato a formare O₃. Come è evidenziato questo processo di fatto rompe l'equilibrio fotostazionario permettendo l'accumulo di O₃.



VOC IN LOMBARDIA



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Maggiori costituenti dei combustibili sia per riscaldamento che per veicoli (fino al 55-65%)

➤ Alcheni



Costituenti minori dei combustibili 5-10% e composti di origine industriale (es. etilene usato nella formazione dei polimeri)

➤ Alchini



Composti di origine industriale

➤ CFC e composti clorurati



Protocollo Montreal

➤ Aromatici



Costituenti delle benzine e utilizzati come solventi

➤ Carbonili



- emissioni dirette
- formazione per via fotochimica

Measurements of Ozone Precursors in Urban Areas and at Highways, Th. Schimitz, D. Klemp and D. Kley, Eurotrac Symposium '98.



COMPOSTI CAMPIONATI

LOCALITA' I CAMPIONAMENTO	etene	propene	i-butene	1-pentene	allene	trans-2-butene	cis-2-butene	2-metil-2-butene	cis-3-esene	3-metil-1-butene
Valmasino	1,01	0,31	0,07	0,03	0,00	0,00	0,00	0,01	0,037	0,000
Iseo	3,90	1,09	0,12	0,04	0,05	0,04	0,04	0,03	0,137	0,000
Fiume Oglio	9,80	2,71	0,37	0,13	0,17	0,26	0,22	0,18	0,026	0,055
Sondrio	17,11	4,93	0,70	0,32	0,28	0,62	0,51	0,44	0,057	0,120
Lecco	93,33	29,07	5,32	2,62	2,10	5,26	4,35	4,06	0,301	1,011
Varenna	5,48	1,74	0,25	0,10	0,11	0,13	0,12	0,11	0,039	0,048
Bergamo	12,57	3,48	0,62	0,33	0,25	0,53	0,47	0,43	0,134	0,119
Bergamo (zona ind.)	23,31	6,26	1,03	0,50	0,40	0,80	0,68	0,57	0,164	0,182
Brescia	13,80	3,49	0,42	0,15	0,17	0,25	0,21	0,14	0,329	0,060
Milano	91,33	23,06	4,17	2,17	1,58	3,28	2,84	2,32	0,000	0,747
Milano 20 m	33,96	8,41	1,43	0,81	0,55	1,34	1,01	0,85	1,296	0,274
Bresso	61,01	16,12	2,60	1,27	1,16	2,35	2,04	1,31	0,880	0,470
Agrate (zona ind.)	33,50	9,24	1,43	0,69	0,60	1,19	0,99	0,77	0,403	0,233
Parabiago	70,48	18,64	2,80	1,32	1,48	2,41	2,05	1,69	0,000	0,489
Parabiago 20 m	38,53	9,81	1,48	0,70	0,66	1,26	1,08	0,77	0,863	0,274
Varese	39,71	10,56	1,91	0,87	0,71	1,47	1,32	1,11	0,173	0,337
Lurate Caccivio (ind.)	14,95	3,78	0,64	0,33	0,25	0,50	0,43	0,40	0,608	0,109
Como/CH	18,51	5,13	0,81	0,31	0,30	0,49	0,43	0,34	0,102	0,126
Cremona	99,37	25,81	3,98	1,40	2,03	2,83	2,37	1,83	0,274	0,596
Cremona (zona ind.)	80,66	23,22	5,97	2,16	1,64	7,35	6,00	2,92	0,469	1,036
Mantova	24,49	6,77	1,01	0,31	0,41	0,72	0,68	0,38	0,280	0,141
Mantova (zona ind.)	7,42	2,07	0,36	0,12	0,09	0,13	0,12	0,09	0,315	0,045
Lodi	122,60	39,59	5,66	2,72	2,55	5,43	5,04	3,74	0,353	0,996
Pavia	53,21	18,75	3,99	2,00	1,19	2,96	2,63	2,55	0,245	0,773
media	40,42	11,42	1,96	0,89	0,78	1,73	1,48	1,13	0,31	0,34

The alkenes react with the OH radical, the NO₃ radical, and O₃. The room temperature rate constants for the reactions with the OH radical are in the range $(1-10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with the monoterpenes being somewhat more reactive. The room temperature rate constants for the NO₃ radical reactions range from $\sim 2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $\sim 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with certain of the monoterpenes being still more reactive. The room temperature rate constants for the O₃ reactions range from $\sim 1 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $\sim 4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with certain of the monoterpenes being still more reactive.

Combining these rate constants for the OH and NO₃ radical reactions with ambient tropospheric OH and NO₃ radical and O₃ concentrations of $1.6 \times 10^6 \text{ molecule cm}^{-3}$ (12-hr daytime average), $5 \times 10^8 \text{ molecule cm}^{-3}$ (12-hr nighttime average) and $7 \times 10^{11} \text{ molecule cm}^{-3}$ (24-hr average), respectively, leads to calculated lifetimes of the alkenes due to OH radical and NO₃ radical and O₃ reaction of 0.1-2 days, 0.005-200 days, and 0.1-10 days, respectively.

Calculated Tropospheric Lifetimes of Selected Alkenes
Due to Reaction with OH Radicals, NO₃ Radicals and O₃

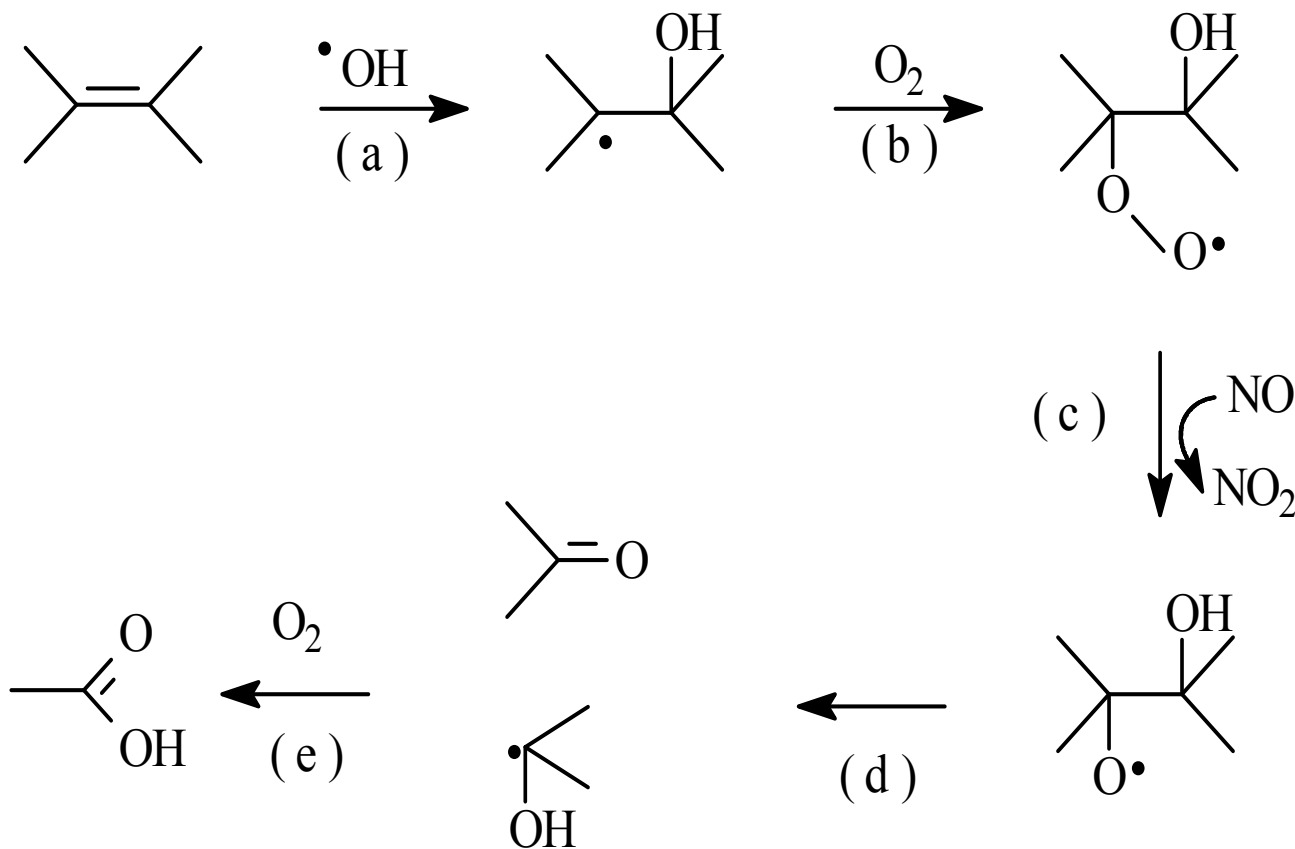
Alkene	Lifetime Due to Reaction with ^a		
	OH	NO ₃	O ₃
Ethene	1.7 days	230 days	10 days
Propene	6.6 hr	4.9 days	1.6 days
<u>trans</u> -2-Butene	2.7 hr	1.4 hr	2.1 hr
Isoprene	1.7 hr	0.8 hr	1.3 days
Limonene	1.0 hr	0.05 hr	1.9 hr

^aUsing the concentrations of OH radicals, NO₃ radicals and O₃ given in the text.

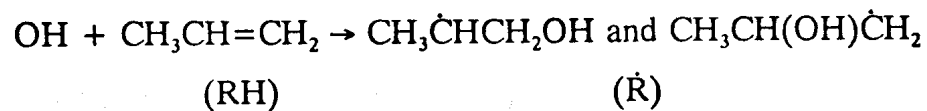
OH RADICAL REACTION

In urban areas, the concentrations of NO_x are generally sufficiently high that the dominant reactions of peroxy radicals [HO_2 and organic peroxy (ROO) radicals] are with NO . The simplest alkenes react in a manner similar to methane and the alkanes, except that the OH radical reactions proceed by initial addition of the OH radical to the $>\text{C}=\text{C}<$ bond.

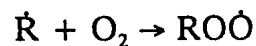
Viene mostrata a titolo di esempio la reazione dell'*etilene*: nello passaggio (a) si può vedere l'addizione diretta al sistema π (a), cui segue l'addizione di ossigeno al radicale alchilico risultante, che genera l' α -idroperossoradicale (b), il passaggio successivo (c) conduce per scissione omolitica ad un α -idrossoalcoosso, la cui rottura (d) porta alla formazione di formaldeide e quindi acido formico (e):



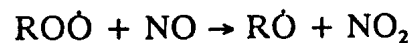
Taking propene, $\text{CH}_3\text{CH}=\text{CH}_2$, as an example, then



where $\dot{\text{R}}$ is a β -hydroxyalkyl radical in this case. These β -hydroxyalkyl ($\dot{\text{R}}$) radicals then react with O_2 and then NO ,

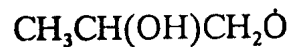
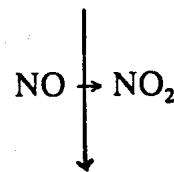
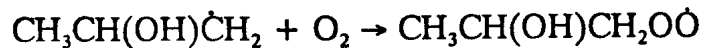


where $\text{RO}\dot{\text{O}}$ is a β -hydroxyalkyl peroxy radical,

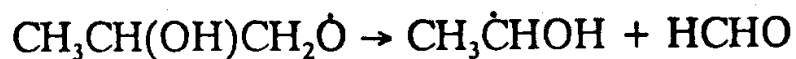
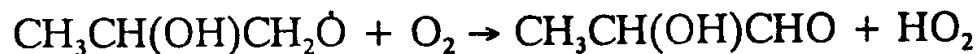


leading to the formation of an β -hydroxyalkoxy ($\dot{\text{R}}$) radical.

For example:

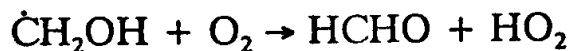
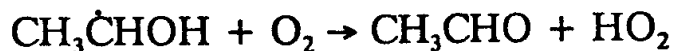


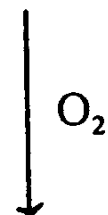
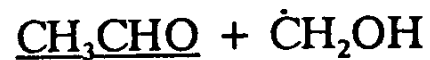
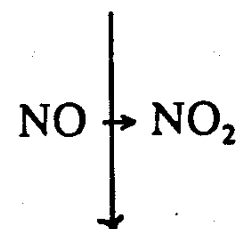
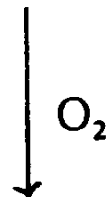
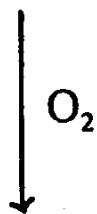
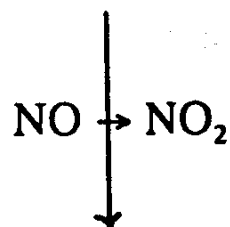
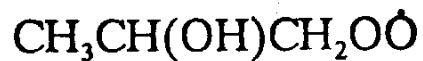
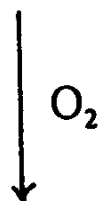
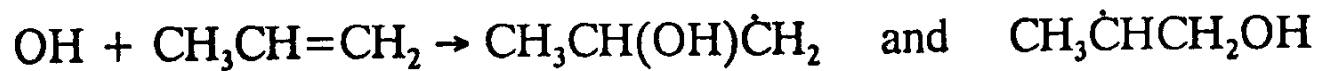
As for the alkoxy radicals formed from the alkanes, these β -hydroxyalkoxy radicals can react with O_2 or decompose.



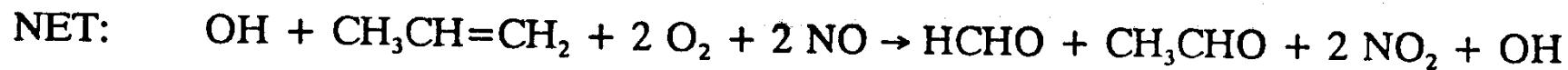
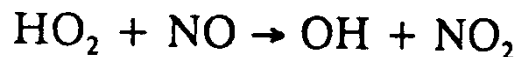
Under atmospheric conditions the β -hydroxyalkoxy radicals formed from ethene, propene and the other methyl-substituted ethenes decompose rather than react with O_2 .

The α -hydroxy radicals such as $CH_3\dot{C}HOH$ and $\dot{C}H_2OH$ react rapidly (and only) with O_2 under tropospheric conditions





followed by regeneration of the OH radical



and these OH radical reactions proceed by "breaking" the $>\text{C}=\text{C}<$ bond to form two carbonyl compounds.



Per quanto riguarda i composti di origine vegetale è riportata la reattività dell'*isoprene*, che essendo un diene presenta due regiochimiche di attacco per il radicale $\text{OH}\cdot$, questo determina la formazione di due diversi α -idroperossoradicali che, in presenza di NO , generano due diversi idrossinitrati (a) ed enedioli isomeri (b). Questi ultimi prodotti, in condizioni troposferiche, si trasformeranno in α -idrossoalcossoradicali, i quali andranno a formare, come evidenziato in studi di laboratorio, composti idrocarbonilici come il 2- metil-4-idrossi-but-1-en-3-one e il 1-idrossi-2-metilbut-2-enale , nonché il 3-metilfurano:

