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FREE RADICALS IN THE ATMOSPHERE

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Like the oxidation in a flame, the oxidation in the atmosphere is mediated by free radicals. Unlike a flame, however, atmospheric oxidation needs an external source of energy: the sun light. In fact the most important radical acting in the lower atmosphere, the hydroxyl radical, OH, is produced following the UV-photolysis of ozone, O_3, which yields an excited oxygen atom, O^1D:

$$O_3 + h\nu \rightarrow \cdot O^1D + O_2; \quad \lambda \leqq 320\,\text{nm}$$

$$\cdot O^1D + H_2O \rightarrow \cdot OH + \cdot OH$$

OH reacts with most atmospheric trace gases, in many cases as the first and rate determining step in the reaction chain leading to oxidation. In this way a host of various other radicals (e.g. peroxy radicals), most of them very short lived, are generated. Usually these oxidation reactions form chains which regenerate OH, thus maintaining OH at a relatively high concentration level on the order of $10^6\,\text{cm}^{-3}$ during the day. The reactions which control the OH concentration will be discussed in detail. During the night radical formation is greatly diminished. It proceeds, for example, through the reaction of olefines with O_3, and, in dry air, through reaction of olefines and aldehydes with the nitrate radical, NO_3.

KEY WORDS: Photochemistry, troposphere, hydroxyl radical.

INTRODUCTION

It is by now well recognized that free radicals play a very important role in the chemistry of all regions of the atmosphere: in the stratosphere as well as in the troposphere, in polluted and clean air, and in cloud droplets and precipitation as well as in the gas phase. In the following I will concentrate on the gas phase chemistry of the troposphere, i.e. the chemistry of the lowest 10 km of the atmosphere, which form the immediate envelope of the biosphere and thus may be of most interest presently. Obviously, the troposphere is that part of the atmosphere which is most strongly influenced by the emissions of trace species and pollutants at the earth's surface by both the biosphere and man's activities. The chemical composition of the troposphere, therefore, includes a complex mix of trace gases. Although, the concentrations of these trace gases remain small and may appear unimportant, their effect on the chemical and radiative state of the atmosphere is not: in fact the chemistry in the troposphere is controlled by the trace gases, since there the major components, namely N_2 and O_2, are photochemically unreactive. As it turns out most of the trace gases are being oxidized and eventually removed from the atmosphere via radical reactions. The most important of these reactions are those with the hydroxyl radical, OH, and the major part of this paper will be devoted to the discussion of the salient features of the OH chemistry. However radical forming reactions of olefins with ozone, O_3, and – night-time – reactions initiated by the nitrate radical, NO_3, also play a role and will be touched upon briefly.

THE BASIC FEATURES OF TROPOSPHERIC OH CHEMISTRY

The production of OH in all but the most polluted situations is initiated by the photolysis of O_3:

$$O_3 + h\nu \rightarrow \cdot O^1D + O_2 \qquad \lambda \leq 320\,\text{nm} \tag{1}$$

At wavelengths below 320 nm an excited oxygen atom, O^1D, is formed in the O_3 photolysis with an energy of about 2 eV above groundstate. That O^1D atom can react with water vapor, H_2O, to form OH radicals.

$$\cdot O^1D + H_2O \rightarrow \cdot OH + \cdot OH \tag{2}$$

And although much of the O^1D is quenched by collisions with N_2 and O_2 to the groundstate, O^3P,

$$\cdot O^1D + N_2 \rightarrow \cdot O^3P + N_2 \tag{3}$$

$$\cdot O^1D + O_2 \rightarrow \cdot O^3P + O_2 \tag{4}$$

up to about 10% of the O^1D formed produce OH, because H_2O is present in the lowest atmosphere with a mixing ratio of about 1% and reaction (2) has a rate constant which is a factor 10 faster than those of reactions (3) and (4) (see Table I).

Incidentally, the solar radiation below 320 nm, which is required for reaction (1), is also responsible for sunburn. Thus one can judge from personal experience, when and where O^1D production is most intense. The O_3 required is also virtually ubiquitous. In the remote background atmosphere it is mainly provided by slow downward transport from the stratosphere and maintained at a mixing ratio of 20 to 40 ppb (parts per billion by volume, 10^{-9}). The chemistry of OH shows two features which allow it to build up to concentrations on the order of $10^6\,\text{cm}^{-}$, at which it becomes the most important oxidizing agent in the atmosphere: first, despite its high reactivity towards trace gases, it does not react with any of the major components of air, i.e. N_2, O_2, Ar, H_2O, CO_2. Second, OH is not consumed in its reactions with trace molecules, but regenerated in various catalytic cycles. Both factors limit the net losses of OH considerably.

I would like to illustrate the second point with the most simple example possible, the oxidation of CO by OH.

$$CO + \cdot OH \rightarrow CO_2 + H\cdot \tag{5}$$

Upon reaction with OH, CO is immediately converted to the stable end product CO_2; in addition a hydrogen atom is formed. The latter – being highly reactive – quickly combines (in a three body collision) with an O_2 molecule to form the hydroperoxy radical, HO_2:

$$\cdot H + O_2 + M \rightarrow HO_2\cdot + M \tag{6}$$

where M stands for N_2 or O_2, the most abundant air molecules. This is an important step, because it activates so to speak the atmospheric O_2. $HO_2^{\cdot}$ is much more reactive than O_2 and oxidizes molecules which cannot react with molecular O_2 at tropospheric temperatures. In particular $HO_2^{\cdot}$ does react with nitrogen monoxide, $NO^{\cdot}$:

TABLE I
Elementary reactions and their rate constants utilized in the calculation of tropospheric OH (temperature 298 K; pressure 1 atm; De More *et al.*, 1985; the photolysis rates are those measured on May 20, 1983, 9:08–11:30 AM, Deuselbach, Hunsrück, FRG)

photolysis		photolysis frequency (s^{-1})
$O_3 + h\nu$	$\rightarrow O^1D + O_2\ \lambda \leqq 310$	1.1×10^{-5}
$NO_2 + h\nu$	$\rightarrow NO + O$	6.5×10^{-3}
$CH_2O + h\nu$	$\rightarrow CO + H_2$	7.8×10^{-5}
$CH_2O + h\nu$	$\rightarrow HCO + H$	2.0×10^{-5}
$H_2O_2 + h\nu$	$\rightarrow OH + OH$	8.4×10^{-6}
heterogeneous loss (wash out, collision with aerosol)		frequency (s^{-1})
HNO_3		1.1×10^{-5}
H_2O_2		1.1×10^{-5}
gas phase reactions		rate constants ($cm^3\ molec^{-1} s^{-1}$)
$O^1D + H_2O$	$\rightarrow OH + OH$	2.2×10^{-10}
$O^1D + N_2$	$\rightarrow O^3P + N_2$	2.6×10^{-11}
$O^1D + O_2$	$\rightarrow O^3P + O_2$	4.0×10^{-11}
$OH + O_3$	$\rightarrow HO_2 + O_2$	6.8×10^{-14}
$OH + H_2O_2$	$\rightarrow HO_2 + H_2O$	1.7×10^{-12}
$OH + H_2$	$\rightarrow H + H_2O$	6.7×10^{-15}
$OH + NO_2 + M$	$\rightarrow HNO_3 + M$	1.16×10^{-11}
$OH + CO$	$\rightarrow H + CO_2$	2.4×10^{-13}
$OH + CH_4$	$\rightarrow CH_3 + H_2O$	7.7×10^{-15}
$OH + CH_2O$	$\rightarrow HCO + H_2O$	1.0×10^{-11}
$OH + CH_3O_2H$	$\rightarrow CH_3O_2 + H_2O$ (?)	1.0×10^{-11}
$OH + OH$	$\rightarrow H_2O + O$	1.9×10^{-12}
$OH + OH + M$	$\rightarrow H_2O_2 + M$	3.9×10^{-12}
$OH + HO_2$	$\rightarrow H_2O + O_2$	1.1×10^{-10}
$OH + SO_2 + M$	$\rightarrow HSO_3 + M$	8.9×10^{-13}
$H + O_2 + M$	$\rightarrow HO_2 + M$	1.2×10^{-12}
$HO_2 + O_3$	$\rightarrow OH + O_2 + O_2$	2.0×10^{-15}
$HO_2 + HO_2$	$\rightarrow H_2O_2 + O_2$	4.6×10^{-12}
$HO_2 + NO$	$\rightarrow OH + NO_2$	8.3×10^{-12}
$H_2 + CH_3O_2 + M$	$\rightarrow CH_3O_2H + O_2 + M$	5.9×10^{-12}
$O + O_2 + M$	$\rightarrow O_3 + M$	1.4×10^{-14}
$O_3 + NO$	$\rightarrow NO_2 + O_2$	1.8×10^{-14}
$HCO + O_2$	$\rightarrow CO + HO_2$	5.5×10^{-12}
$CH_3 + O_2 + M$	$\rightarrow CH_3O_2 + M$	1.1×10^{-12}
$NO_2 + O_3$	$\rightarrow NO_3 + O_2$	3.2×10^{-17}
$HSO_3 + O_2$	$\rightarrow HO_2 + SO_3$	4.0×10^{-13}
$CH_3O_2 + NO$	$\rightarrow CH_3O + NO_2$	7.6×10^{-12}
$CH_3O + O_2$	$\rightarrow HO_2 + CH_2O$	1.5×10^{-15}
$NO_2 + NO_3$	$\rightleftharpoons N_2O_5$	

$$HO_2^{\cdot} + \cdot NO \rightarrow \cdot OH + \cdot NO_2 \qquad (7)$$

Incidentally, at northern midlatitudes, reaction (7) is by far the most important reaction path for $HO_2^{\cdot}$.

More important for our present consideration is the fact, that reaction (7) regenerates the OH which was invested in reaction (5) to oxidize CO.

Another important point is that the nitrogen dioxide radical, $NO_2^{\cdot}$ also produced in reaction (7), is photolyzed by the solar radiation penetrating to the troposphere:

$$\cdot NO_2 + h\nu \rightarrow \cdot NO + \cdot O^3P \qquad (8)$$

giving back NO˙ and an oxygen atom which quickly combines with O_2 to form O_3:

$$\cdot O + O_2 + M \rightarrow O_3 + M \qquad (9)$$

Combining the elementary reactions (5)–(9), we obtain the net reaction:

$$CO + 2O_2 + h\nu \rightarrow CO_2 + O_3 \qquad (10)$$

Clearly, OH, HO_2, and NO, NO_2 catalyze the oxidation of CO to CO_2 without being themselves consumed: the reaction chain (5)–(9) can proceed many times before it is terminated by other, radical consuming reactions. Another important consequence is that O_3 is formed in this cycle. This simple cycle already demonstrates the basic features of the photochemical smog reaction: a fuel gas, CO, is photochemically oxidized via OH. In the presence of NO, ozone is generated – at a rate of one O_3 per CO consumed.

Incidentally, by reactions (5)–(9) and other chains of similar kind, OH and HO_2 are interconverted within seconds. Thus both radicals are often lumped together and called HO_x.

At this point it may be useful to briefly digress and illustrate an important feature of the NO and NO_2 radical family, namely its control over the tropospheric O_3 formation.

Besides reaction (7) there is another reaction which converts HO_2 to OH:

$$HO_2\cdot + O_3 \rightarrow OH + 2O_2 \qquad (11)$$

Thus, even without the presence of NO, OH would be recycled. However the complete reaction chain consisting now of (5), (6), and (11) results in the net reaction:

$$CO + O_3 \rightarrow CO_2 + O_2 \qquad (12)$$

i.e. in the destruction of O_3.

The two net reactions (10) and (12) exemplify in a rather straight forward manner the NO_x controlled switch from O_3-destruction to O_3-production. Since the rate constant for the reaction (7) of HO_2 with NO is about 4000 times larger than that of reaction (11) of HO_2 with O_3, and since the O_3 mixing ratio averages less than 40 ppb, an NO mixing ratio of 0.01 ppb is sufficient to cause a net production of O_3. This value is virtually always exceeded in the highly industrialized midlatitudes of the northern hemisphere causing an O_3 production in all seasons.

Returning to the HO_x radicals we note that the peroxy radicals, e.g. HO_2, also play a crucial role in O_3 formation. They are responsible for the transfer of the O-atom to NO to yield NO_2, e.g. reaction (7), and thus ultimately for the oxidant formation ending in O_3 as the longest lived oxidant species. There is another interesting feature in some of the HO_x catalyzed oxidation cycles of trace molecules: at the high NO_x concentrations at northern midlatitudes there may even be a net gain of HO_x radicals. The simplest example is offered by the oxidation chain of CH_4 which is also initiated by OH:

$$CH_4 + \cdot OH \rightarrow \cdot CH_3 + H_2O \qquad (13)$$

The OH radical abstracts an H-atom and forms a water molecule, H_2O. The remaining methyl radical, $CH_3^{\cdot}$, reacts extremely fast with molecular oxygen:

$$\cdot CH_3 + O_2 + M \rightarrow CH_3O_2\cdot + M \qquad (14)$$

In analogy to the H-atom in reaction (6) it forms a peroxy radical, the methyl peroxy radical, CH_3O_2. And analogously to HO_2, CH_3O_2 also oxidizes NO:

$$CH_2O_2\cdot + \cdot NO \rightarrow CH_3O\cdot + \cdot NO_2 \qquad (15)$$

The methoxy radical thus formed reacts quickly again with the abundant O_2 and yields formaldehyde, H_2CO:

$$CH_3O\cdot + O_2 \rightarrow H_2CO + HO_2\cdot \qquad (16)$$

The HO_2 radical formed in reaction (16) together with reaction (7) closes the HO_x radical cycle.

Formaldehyde is the first intermediate product of the CH_4 oxidation with a relatively long chemical lifetime in the atmosphere. In the sunlit atmosphere it lives for a few hours and therefore can reach mixing ratios of up to 0.5 ppb even in the clean atmosphere. Eventually also H_2CO reacts further. It is attacked by the OH radical and it is photolysed by solar radiation in the near UV:

$$H_2CO + \cdot OH \rightarrow H\dot{C}O + H_2O \qquad (17)$$

$$H_2CO + h\nu \begin{array}{l} \rightarrow H_2 + CO \qquad (18a) \\ \rightarrow H\dot{C}O + H\cdot \qquad (18b) \end{array}$$

The formyl radical, $HCO^{\cdot}$, generated in reactions (17) and (18b) quickly reacts with O_2:

$$H\dot{C}O + O_2 \rightarrow HO_2^{\cdot} + CO \qquad (19)$$

Thus the HO_x radical consumed in reaction (17) is regenerated.

Moreover there is a net gain of HO_x radicals. In the photolytic decomposition of H_2CO, channel (18b), there are two radicals formed, namely $HCO^{\cdot}$ and $H^{\cdot}$, which quickly convert to $HO_2^{\cdot}$ via reactions (6) and (19). Since in the lower troposphere this channel contributes about 15% to the H_2CO destruction, the net gain amounts to 0.3 HO_2 radicals per CH_4 molecule (or H_2CO molecule) consumed. With other words during the oxidation of CH_4 the number of HO_x radicals is increased. This oxidation chain serves as a radical amplifier. The same is true for the oxidation of other alkanes.

We also note from the example of CH_4 that the oxidation of hydrocarbons initiated by OH leads to the generation of additional radical species i.e. CH_3, CH_3O_2, HCO. This observation can also be generalized to the other alkanes.

So far we have only considered the reactions of OH with molecules. They essentially lead to a conversion of OH to HO_2, i.e. they conserve HO_x. In addition there are a number of radical-radical reactions, which lead to a net loss of HO_x radicals and to a termination of the oxidation chains. These reactions include:

$$\cdot OH + HO_2\cdot \rightarrow H_2O + O_2 \qquad (20)$$

$$HO_2\cdot + HO_2\cdot \rightarrow H_2O_2 + O_2 \qquad (21)$$

which are responsible for the loss of HO_x radicals in clean air and for the H_2O_2 production everywhere. In polluted air the addition of OH to NO_2 forming nitric acid, HNO_3,

TABLE II
Concentrations of the most important trace constituents reacting with OH on May 20, 1983, 9:08–11:30 AM, Deuselbach, Hunsrück, FRG.

Trace gas	Mixing Ratio (ppb)	Concentration (cm^3)
O_3	53	1.32×10^{12}
H_2O	9.1×10^6	2.27×10^{17}
CO	260	6.5×10^{12}
CH_4	1740	4.4×10^{13}
H_2	600	1.5×10^{13}
SO_2	1.6	4×10^{10}
NO	0.5	1.3×10^{10}
NO_2	1.6	4×10^{10}
CH_2O	0.5	1.3×10^{10}

$$\cdot OH + \cdot NO_2 + M \rightarrow HNO_3 + M \tag{22}$$

is the dominant mechanism for HO_x loss.

The reactions (1)–(22) constitute the major production, loss, and interconversion mechanisms of HO_x. With their help the tropospheric concentration of OH can be estimated in reasonable approximation. They are summarized together with their rate constants in Table I. Obviously the reaction scheme is still incomplete; it does — for

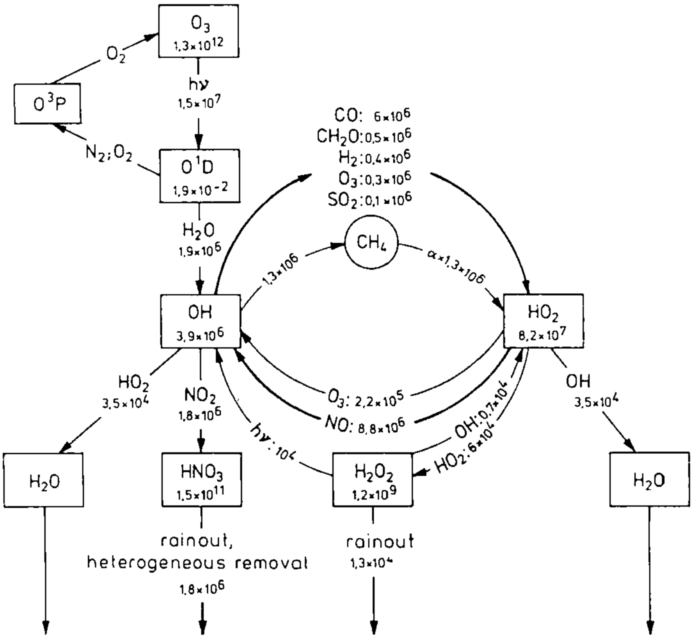


FIGURE 1 The HO_x reaction cycle.[4] The numbers in the boxes represent the calculated concentrations (in molecules/cm^3); the numbers in the arrows represent the reaction rates (in molecules/cm^3/s) with the indicated trace species for an air parcel observed on May 20, 1983, 9:08–11:30 AM, at Deuselbach (see text and Tables I, II).

example – not include the light non-methane hydro-carbons (NMHC). However, in general the impact of NMHC on the OH concentration is relatively small, although their influence on the HO_2 concentration can be considerable. to estimate the OH concentration from the reaction scheme presented we consider an actual situation where the concentrations of most trace molecules reacting with OH, as well as OH itself had been measured. These concentrations are listed in Table II. The field experiment on May 20, 1983, 9:08–11:30 AM, which yielded these data also provided empirical photolysis rates. They are included in Table I. With these measurements the air mass is more or less characterized chemically and its OH, HO_2 and H_2O_2 can be calculated by a numerical model of the atmospheric chemistry. The results are shown in the flow diagram of Figure 1 which also indicates the important reaction paths and their conversion rates.

Clearly, photolysis of O_3 followed by the reaction of O^1D with H_2O is the dominant source of HO_x with a rate of $1.9 \times 10^6 \, OH \, cm^{-3} sec^{-1}$. A second but significantly lower source of HO_x is the photolysis of H_2CO produced in the oxidation of CH_4: it is indicated by the factor α and amounts to about 10% of the primary OH formation.

The production of HO_x is balanced by a net destruction which proceeds mainly through the reaction (22) of OH with NO_2, since the NO_2 concentration was relatively high: 1.6 ppb. In the present case the destruction via reactions between the HO_x radicals amount to only 5% of the total HO_x removal.

Despite the fast net removal of OH by NO_2 the major part of the OH is first converted to HO_2-mainly through the reaction with CO, which contributes 66% of the total conversion rate of $9 \times 10^6 \, OH \, cm^{-3} sec^{-1}$. The ratio of the HO_x conversion to HO_x destruction rate is 5. That means that a HO_x conversion to HO_x destruction rate is 5. That means that a HO_x radical is cycled five times between OH and HO_2 before it is removed from the atmosphere by reaction (22) with NO_2.

The corresponding time constants are obtained by division of the concentrations by the reaction rates. Thus, in the present example, an OH is converted to HO_2 every O.4 sec, an HO_2 radical is converted to OH every 9 sec, and the mean life time of an HO_x radical with respect to net removal is 45 sec.

Using our simplified set of reactions an OH concentration of $3.9 \times 10^6 cm^{-3}$ is estimated. A more complete calculation including the chemistry of the non methane hydrocarbons gave $4.3 \times 10^6 cm^{-3}$.

The last two numbers illustrate that the concentration of the OH radical is controlled by a relatively small number of reactions despite its numerous interactions with all kinds of other trace molecules. Obviously the controlling reactions are those with the highest conversion rates i.e. those, where the reactants are supplied in high concentrations and react quickly with OH. These are essentially those reactions I had chosen to illustrate the basic function of the HO_x cycle. They establish a chemical system which maintains a certain OH concentration which is then available for the removal of other trace gases as well. Because of their relatively low rates the reactions of these additional gases feed only weakly back to the OH concentration.

Platt *et al.*[12] show that the OH concentrations measured so far do not agree all that well with the model predicted values, which indicates certain short-comings in our understanding of the tropospheric OH chemistry. Nevertheless, the measurements do confirm that OH is present in concentrations to the order of $10^6 cm^{-3}$. At those concentrations OH is by far the most efficient oxidizing agent in the atmosphere. In many cases it forms the first and rate determining step in the reaction chain leading

TABLE III

The global budget of selected tropospheric trace gases and the relative role of OH in their removal. The average global OH concentration is assumed to be $0.6 \times 10^6 cm^{-3}$ (Volz *et al.*, 1981).[16] Examples of the radicals formed in the oxidation chain initiated by OH are indicated in the right column

Trace gas	Global Budget (million tons per year)	Oxidation by OH (percent)	Radicals produced
CO	2800	≥ 90 1)	$HO_2\cdot$
CH_4	500	≥ 90 2)	$HO_2\cdot$, $\cdot CH_3$, $CH_3O\cdot$, $CH_3O_2\cdot$, $H\dot{C}O$
Alkanes	20	≥ 90 3)	$HO_2\cdot$, $R\cdot$, $RO\cdot$, $RO_2\cdot$, $R\text{-}\dot{C}C$, $RCOO_2\cdot$
Isoprene	350	≥ 90 4)	+ corresponding hydroxy alkyl radicals
Terpenes	480	≥ 50 4)	
NO_2	160	≥ 50 5)	None
SO_2	300	≥ 30 6)	$H\dot{S}O_3$, $\cdot SO_3$, $HO_2\cdot$
$(CH_3)_2S$	80	≥ 90 7)	$CH_3S\dot{C}H_2$, $CH_3SCH_2OO\cdot$, $CH_3SCH_2\dot{O}$, $CH_3S\cdot$

1) Volz *et al.*[16]
2) Ehhalt[3]
3) Ehhalt *et al.*[6]
4) Zimmermann *et al.*[17]
5) Logan[11]
6) Janßen-Schmidt *et al.*[9]
7) Global Tropospheric Chemistry (1984)[7]

to oxidation. Since in the chains new radical species are generated at each reaction step, OH is also the main agent for the formation of all kinds of other radicals. The largest variety of radicals occurs in the oxidation of hydrocarbons. Fortunately, the more abundant radicals can easily be categorized, e.g. the radicals derived from the oxidation of CH_4, discussed above, can be generalized to the higher alkanes. Rhäsa and Zellner[15] present more examples of hydrocarbon radicals. Here, I would just like to remind ourselves, that in the case of alkenes OH reacts differently. Rather than abstracting an H-atom as in the case of alkanes, it breaks the double bond and adds to one of the carbon atoms. This is most easily seen in the oxidation of ethene:[10,2]

$$CH_2{=}CH_2 + OH \rightarrow HOCH_2\text{-}\dot{C}H_2 \tag{23}$$

$$HOCH_2\text{-}\dot{C}H_2 + O_2 \rightarrow HOCH_2\text{-}CH_2O_2^{\cdot} \tag{24}$$

$$HOCH_2\text{-}CH_2O_2^{\cdot} + \cdot NO \rightarrow HOCH_2\text{-}CH_2O\cdot + NO_2^{\cdot} \tag{25}$$

$$HOCH_2\text{-}CH_2O\cdot + O_2 \rightarrow HOCH_2\text{-}CHO + HO_2^{\cdot} \tag{26}$$

$$HOCH_2\text{-}CH_2O\cdot \rightarrow H_2CO + HO\dot{C}H_2 \tag{27}$$

$$HO\dot{C}H_2 + O_2 \rightarrow H_2CO + HO_2\cdot \tag{28}$$

Corresponding to the alkoxy, and alkylperoxy radicals one obtains the hydroxyl substituted hydroxy alkyl, hydroxy alkoxy, etc. radicals.

I have attempted, in Table III, to summarize the impact of OH reaction on the budgets of some of the major trace gases in the troposphere. Table III also lists the radicals formed in the oxidation of these trace gases. We note that some of these gases (especially CO) are cycled at rather high rates through the atmosphere, and that reaction with OH is the most important removal mechanism for all of them, with the exception of SO_2 where – owing to its high solubility – dry and wet deposition play a major role.

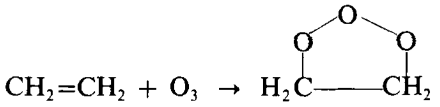
The high trace molecule budgets imply similarly high production rates – or more precisely conversion rates – of radicals. For example in the oxidation of CO 3300×10^6 t of HO_2 are anually generated from OH.

Obviously, the radicals generated along the reaction chains, although formed at the same rates at each reaction step, will have different abundances depending on their respective reactivities. Radicals such as R, or RCO which react with O_2, a very abundant atmospheric molecule, are converted quickly and are present in low concentration. As a consequence the peroxy radicals are generally the most abundant of the radicals listed.

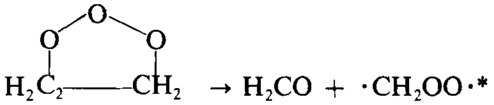
NIGHT-TIME RADICAL CHEMISTRY

So far we have concentrated on the OH chemistry as the most important radical mechanism in the atmosphere. However, there are other radical formation mechanisms, namely the reaction of ozone with olefinic compounds and the reaction of the nitrate radical with organic compounds. In contrast to the photochemistry of OH which requires sunlight, the ozone reactions proceed at day and night, and NO_3, mainly at night. Thus, there is a nighttime radical chemistry which compared to day time proceeds at a greatly reduced pace and is dominated by O_3 and NO_3. It is briefly discussed in the following.

As is well-known, O_3 attacks the double bond of olefins, and in the dilute gas phase eventually forms an aldehyde and an (excited) biradical, the so called Criegee intermediate,[8] e.g.



(29)



(30)

$$\cdot CH_2OO\cdot^* \rightarrow \cdot CH_2OO\cdot \quad (40\%) \qquad (31)$$
$$\rightarrow CO + H_2O \quad (42\%)$$
$$\rightarrow CO_2 + H_2 \quad (12\%)$$
$$\rightarrow CO_2 + 2H\cdot \quad (6\%)$$

In the case of ethene ozonolysis about 40% of the excited Criegee intermediates are stabilized by collisions with air molecules, the remainder decay into CO and HO_2, or CO_2 and H_2 or H respectively. The stabilized Criegee is capable of further reactions,

$$\text{e.g.} \quad \cdot CH_2O_2\cdot + \cdot NO \rightarrow H_2CO + \cdot NO_2 \qquad (32)$$

for which, however, the rate constants are not well-known. In the oxidation of higher alkenes peroxy radicals are formed in low yields,[10] and contribute to radical chemistry, in the same way as shown for CH_3O_2.

TABLE IV

Intercomparison of the reaction rates of various organic trace molecules with OH, O_3, and NO_3. The rate constants are given for 298 K in cm^3 $molecule^{-1}$ s^{-1}. The respective lifetimes are calculated on the basis of following concentrations – OH/ $10^6 cm^{-3}$; O_3: 30 ppb; NO_3: 10 ppt. (after Atkinson et al., 1984)[1]

Organic	rate constants			lifetimes		
	k_{OH}	k_{O_3}	k_{NO_3}	τ_{OH}	τ_{O_3}	τ_{NO_3}
ethene	8.5×10^{-12}	1.8×10^{-18}	6.1×10^{-17}	33 hr	9 days	2.2 yr
propene	2.5×10^{-11}	1.1×10^{-17}	4.2×10^{-15}	11 hr	35 hr	11 days
isoprene	9.6×10^{-11}	1.2×10^{-17}	3.2×10^{-13}	2.9 hr	32 hr	3.6 hr
α-pinene	6×10^{-11}	8.4×10^{-17}	3.4×10^{-12}	4.6 hr	4.6 hr	20 min
n-butane	2.6×10^{-12}	$< 10^{-22}$	2.8×10^{-17}	4.5 days	–	4.7 yr
formaldehyde	1×10^{-11}	– negl.	3.2×10^{-16}	28 hr	–	144 days

Whereas O_3 is nearly always present, the NO_3 radical has to be formed first in the local atmosphere: It is produced exclusively by

$$\cdot NO_2 + O_3 \rightarrow \cdot NO_3 + O_2 \tag{33}$$

This reaction proceeds, of course, also during day time. But during the day NO_3 is photolyzed within tens of seconds

$$\cdot NO_3 + h\nu \rightarrow \cdot NO_2 + \cdot O \tag{34a}$$

$$\rightarrow \cdot NO + O_2 \tag{34b}$$

such that very low concentrations prevail.

At night-time NO_3 can build up to significant concentrations, however; in polluted areas mixing ratios of several hundred ppt have been observed.[14] NO_3 combines with NO_2 to form N_2O_5,

$$\cdot NO_3 + \cdot NO_2 \rightleftharpoons N_2O_5 \tag{35}$$

which thermally decomposes back to NO_3 and NO_2. N_2O_5 reacts with condensed water to form HNO_3. Thus it is expected to rapidly react upon collision with the wet surface provided by aerosol particles at relative humidities above 60%.[5,14] In nights with high humidities this reaction path provides an efficient loss of NO_x. At the same time NO_3 (and N_2O_5) concentrations remain unmeasurably low.[13] Only during dry nights with relative humidities below 60% is NO_3 observed and can act as a significant source of other radicals.

Similar to OH, NO_3 abstracts an H-atom when reacting with alkanes, aromatics or aldehydes.[1] The resulting radicals are thus the same as those of the corresponding OH reactions. The reactions with alkenes proceed via an initial addition of the NO_3 radical to the olefinic double bond,

$$\text{e.g.} \quad CH_2{=}CH_2 + NO_3 \rightarrow \dot{C}H_2\text{–}CH_2ONO_2 \tag{36}$$

Further reactions proceed analogous to the OH initiated reactions (23)–(26) giving nitrate substituted radicals:

$$\dot{C}H_2\text{–}CH_2ONO_2 + O_2 \rightarrow \cdot O_2CH_2\text{–}CH_2ONO_2 \tag{37}$$

$$\dot{O}_2CH_2\text{–}CH_2ONO_2 + \cdot NO \rightarrow \cdot OCH_2\text{–}CH_2ONO + \cdot NO_2 \tag{38}$$

$$\cdot OCH_2\text{–}CH_2ONO_2 + O_2 \rightarrow O_2NOCH_2\text{–}CHO + HO_2^{\cdot} \tag{39}$$

$$\cdot OCH_2\text{-}CH_2ONO_2 \rightarrow 2H_2CO + \cdot NO_2 \tag{40}$$

(Kerr and Calvert, 1984).[10]

We note, however, that the NO molecules required for reaction (38) will hardly be present at night, since generally all NO will have been converted NO_2.

To illustrate the relative importance of OH, O_3 and NO_3 initiated reactions, Table IV lists the respective rate constants of a few important organic molecules. For better intercomparison the corresponding lifetimes of the organic molecules are also given assuming average OH, O_3 and night-time NO_3 concentrations. As Table IV demonstrates reaction with OH is by far the dominant loss process for most of these molecules. However, in certain cases, e.g. α-pinene, reaction with O_3 and NO_3 in particular, might be of equal or greater importance. By the same token daytime chemistry is by far more important than night-time chemistry. Under normal conditions night-time radical concentrations are by a factor of 100 reduced, disregarding of course NO, NO_2 and NO_3 which are always more abundant than HO_x or organic radicals.

CONCLUSION

Using simple but important examples I have tried to illustrate the salient features of tropospheric radical chemistry. As it turns out the OH radical is most important. This is due to its high reactivity and its relatively high concentration due to the recycling of the HO_x radicals. The other radicals formed in the oxidation reactions of various tropospheric molecules do not show that property.

This presentation is neccessarily incomplete, in particular the chemistry of organic molecules is of bewildering complexity and not fully explored, as there are many other details of tropospheric radical chemistry which are not completely understood. But it appears that the basic features of tropospheric radical chemistry are sufficiently well understood to allow its numerical modelling in reasonable approximation. In any case I hope to have set the stage for the following papers, which will also fill in some of the gaps I had to leave.

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