Photochemical reactions in the tropospheric aqueous phase and on particulate matter

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This paper is a *tutorial review* in the field of atmospheric chemistry. It describes some recent developments in tropospheric photochemistry in the aqueous phase and on particulate matter. The main focus is regarding the transformation processes that photochemical reactions induce on organic compounds. The relevant reactions can take place both on the surface of dispersed particles and within liquid droplets (*e.g.* cloud, fog, mist, dew). Direct and sensitised photolysis and the photogeneration of radical species are the main processes involved. Direct photolysis can be very important in the transformation of particle-adsorbed compounds. The significance of direct photolysis depends on the substrate under consideration and on the colour of the particle: dark carbonaceous material shields light, therefore protecting the adsorbed molecules from photodegradation, while a much lower protection is afforded for the light-shaded mineral fraction of particulate. Particulate matter is also rich in photosensitisers (*e.g.* quinones and aromatic carbonyls), partially derived from PAH photodegradation. These compounds can induce degradation of other molecules upon radiation absorption. Interestingly, substrates such as methoxyphenols, major constituents of wood-smoke aerosol, can also enhance the degradation of some sensitisers. Photosensitised processes in the tropospheric aqueous phase have been much less studied: it will be interesting to assess the photochemical properties of Humic-Like Substances (HULIS) that are major components of liquid droplets. The main photochemical sources of reactive radical species in aqueous solution and on particulate matter are hydrogen peroxide, nitrate, nitrite, and Fe(III) compounds and oxides. The photogeneration of hydroxyl radicals can be important in polluted areas, while their transfer from the gas phase and dark generation are usually prevailing on an average continental scale. The reactions involving hydroxyl radicals can induce very fast transformation of compounds reacting with $^{\bullet}OH$ at a diffusion-controlled rate (10^{10} M^{-1} s^{-1}), with time scales of an hour or less. The hydroxyl-induced reactivity in solution can be faster than in the gas phase, influencing the degradation kinetics of water-soluble compounds. Moreover, photochemical processes in fog and cloudwater can be important sources of secondary pollutants such as nitro-, nitroso-, and chloro-derivatives.

1. Introduction

Reactions taking place in the atmosphere are extremely important because they significantly influence the lifetime of many atmospheric components and yield intermediates that often play a key role in atmospheric chemistry, in particular that of the urban environment. For instance, the occurrence of Volatile Organic Compounds (VOCs, such as aliphatic

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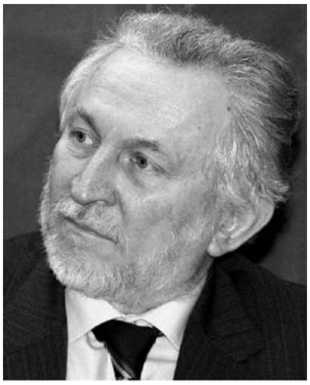

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hydrocarbons, benzene, toluene and xylenes) in urban air is strongly influenced by the emission/degradation budget, where degradation is closely connected to atmospheric reactivity. Moreover, VOC's transformation intermediates are often more harmful to human health and the environment than the parent compounds. Also the occurrence of tropospheric ozone, an important urban pollutant, is the consequence of a complex chain of atmospheric processes involving solar radiation, VOC, and nitrogen oxides (NO_x). Gas-phase atmospheric reactions have been extensively studied: these include, for instance, direct photolysis of photoactive compounds, and processes initiated by reactive species ($^{\bullet}OH$, $^{\bullet}NO_3$, ozone).[1,2] The importance of atmospheric reactions taking place in the aerosol phase (on particles or in aqueous solution) has been acknowledged more recently. Interest in this area may be largely attributed to the discovery that the Antarctic stratospheric ozone hole is caused by reactions occurring on the surface of the crystals composing the Polar Stratospheric Clouds. Further research has highlighted the importance of many chemical processes taking place in the tropospheric aerosol phase. These processes can be categorised as either "heterogeneous" reactions, occurring on the surface of tropospheric particles, or "multiphase" reactions, taking place on the surface or inside water droplets.[3] Examples include the conversion of $^{\bullet}NO_2$ into HNO_2 on the surface of soot particles[4] (HNO_2 photolysis is then one of the processes that initiate the tropospheric ozone cycle), the oxidation of S(IV) to H_2SO_4 by H_2O_2 in water droplets (H_2SO_4 is involved in the phenomenon of acid rain), and the formation of active chlorine species upon reaction between nitrogen oxides and sea-salt particles. A series of processes that need further investigation include:[3] oxidation reactions initiated by aqueous HNO_3, processes (*e.g.* ozone uptake) taking place within organic liquids (such as the ones present on the surface of organic particulate matter), and reactions on mineral oxides/dust. The latter can involve conversion of $^{\bullet}NO_2$ into nitrate and nitrous acid, and oxidation of SO_2.

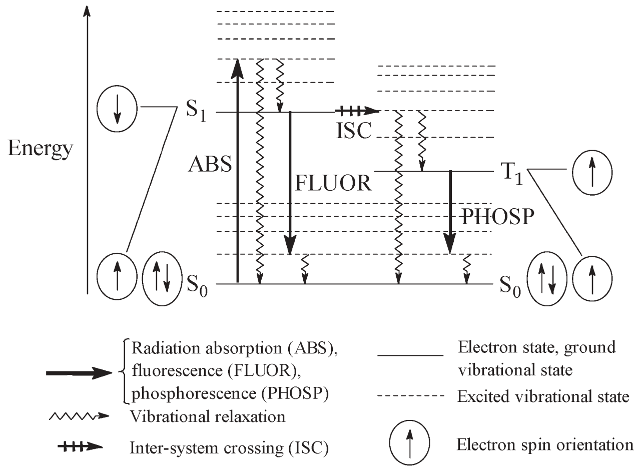
Meanwhile, a growing amount of knowledge has been gathered regarding a class of reactions occurring in the tropospheric aerosol phase: namely photochemical reactions. Initiated by an interest in the photolysis of polycyclic aromatic hydrocarbons (PAHs) on particles,[5] such studies have evolved into a reasonably comprehensive framework of environmental knowledge, involving the photochemistry of particles and water droplets. These issues are the subject of the present review, which will focus on some photochemical reactions taking place in the atmosphere, on particles and in aqueous solution. Direct photolysis and photosensitised processes will be discussed, together with photochemical reactions yielding hydroxyl and other radicals. The main focus will be on the photochemical transformation of organic compounds in the tropospheric aerosol phase.

2. A brief introduction to photochemistry

Radiation absorption by a molecule, which will be represented as A–B, in the UV-Vis range induces electron transitions from a ground state to an excited state at higher energy. In other words, photon absorption shifts an electron from a molecular orbital of lower energy to an orbital at higher energy. Assume A–B* to represent the excited molecule. The surplus energy will consist of both electronic and vibrational energy, as the electron would generally be shifted to an excited vibrational level of the higher energy state. Radiationally excited states are usually very unstable and very often undergo fast decay back to the ground state. Typical decay times lie in the range 10^{-9}–10^{-8} s.[6] Various processes account for the energy decay. The surplus energy can be dissipated upon collisions with other molecules: in the case where A–B* is in solution, most collisions will take place with the solvent molecules. The process is named vibrational relaxation, and it is almost always operational to some extent. This means that at least part of the absorbed energy will be lost this way. In many cases, it happens that all the energy is lost *via* vibrational relaxation. Energy dissipation can also occur upon emission of radiation. Depending on the features of the process, radiation emission can take place as fluorescence or phosphorescence. In both cases the emitted photons usually carry less energy than the absorbed ones, because some of the energy has been vibrationally lost; the main macroscopic difference is that energy decay by fluorescence is faster than by phosphorescence. Fluorescence involves photochemical electronic excitation from the ground singlet state (S_0) to an excited vibrational level of an upper singlet state (*e.g.* S_1). The electron may follow vibrational relaxation to the ground vibrational level of S_1, and upon fluorescence emission falls to an excited vibrational level of S_0, finally undergoing vibrational relaxation to the ground vibrational level of S_0 (see Scheme 1). The singlet–singlet transitions involved in fluorescence are relatively fast. With respect to phosphorescence, after electronic excitation to S_1 and vibrational relaxation, there follows an inter-system crossing to an excited vibrational level of the first excited triplet state (T_1), plus vibrational relaxation to the ground vibrational level of T_1. The T_1 states are longer lived than S_1 because the probability of T_1–S_0 transitions (phosphorescence emission) is much lower when compared with S_1–S_0 (fluorescence emission). After phosphorescence emission the electron reaches an excited vibrational level of S_0, from where it reaches the ground level by vibrational relaxation (Scheme 1). The ground electronic level is usually a singlet (S_0) because most organic molecules have an even number of electrons, all distributed in pairs in the orbitals with antiparallel spins (singlet state). The excited electron in S_1 has maintained its spin orientation, while transition to T_1 implies an inversion in the spin orientation. The T_1–S_0 transition involves spin inversion as well as radiation emission (Scheme 1).

An excited molecule A–B* can also dissipate its surplus energy by direct photolysis and by energy transfer to other molecules. They are the most important energy dissipation pathways for atmospheric reactivity. Photolysis is the breaking of a chemical bond, induced by radiation absorption. Since the surplus energy of A–B* consists of both electronic and vibrational energy, it is possible that the vibrational energy is sufficiently large to induce the breaking of a chemical bond, *i.e.* photolysis (reactions 1–3; $h\nu$ = incident photon, reaction 2 represents complete vibrational relaxation).

$$\text{A–B} + h\nu \rightarrow \text{A–B}^* \quad (1)$$



Scheme 1 Processes that follow photon absorption by a molecule (excluding chemical reactivity): vibrational relaxation, fluorescence, phosphorescence.

$$\text{A–B}^* \rightarrow \text{A–B} + \text{heat} \tag{2}$$

$$\text{A–B}^* \rightarrow \text{A}^\bullet + \text{B}^\bullet \tag{3a}$$

$$\text{A–B}^* \rightarrow \text{A–B}^{+\bullet} + e^- \tag{3b}$$

Photolysis reactions often yield radical species *via* homolytic bond breaking (reaction 3a). In other cases direct or assisted photoionisation is observed (reaction 3b). Moreover, the photolytic process is characterised by its probability to take place. The ratio of the number of molecules that actually undergo photolysis to the number of molecules that have absorbed photons is called the photolysis quantum yield, usually indicated as Φ. Φ represents the probability that the absorption of a photon by a molecule A–B will cause its photolysis, and varies from 0 to 1. The quantum yield is a unit that can be defined for all the processes that follow radiation absorption, *e.g.* fluorescence and phosphorescence. Therefore, the higher the quantum yield, the more likely the process is to occur. Vibrational relaxation, fluorescence, phosphorescence, and photolysis are photoinduced processes in competition with one another.

Alternatively, the surplus energy can be transferred to another molecule, say C–D. The latter is called a quencher as it dissipates, usually by collision, the surplus energy of A–B*. It sometimes happens that C–D, after receiving energy by A–B*, undergoes various kinds of processes, including chemical reactions. In such cases A–B is called a photosensitiser, and C–D is said to undergo photosensitised reactions. If a bond breaking within C–D occurs, we say that the molecule undergoes sensitised photolysis. The overall process of sensitised photolysis is depicted in reactions 1, 2, 4 and 5.

$$\text{A–B}^* + \text{C–D} \rightarrow [\text{A–B}\cdot\cdot\text{C–D}]^* \tag{4}$$

$$[\text{A–B}\cdot\cdot\text{C–D}]^* \rightarrow \\ \text{Products (A–B + C}^\bullet + \text{D}^\bullet\text{; A–B–C}^\bullet + \text{D}^\bullet\ \textit{etc.}) \tag{5}$$

There are two further aspects to be considered. The first is that some of the radical species produced upon photolysis are themselves reactive. This is the case for the hydroxyl radical, $^\bullet$OH, which is produced upon photolysis of various compounds and will react with a very wide variety of molecules[7] (see later). The second consideration is that in the natural environment the light source is the sun. In the troposphere, at ground level, sunlight consists of radiation of wavelengths longer than 290 nm. Accordingly, only those molecules absorbing radiation above 290 nm will be directly excited. The other molecules can still undergo photosensitised transformation or react with photoformed reactive species (*e.g.* the hydroxyl radical).

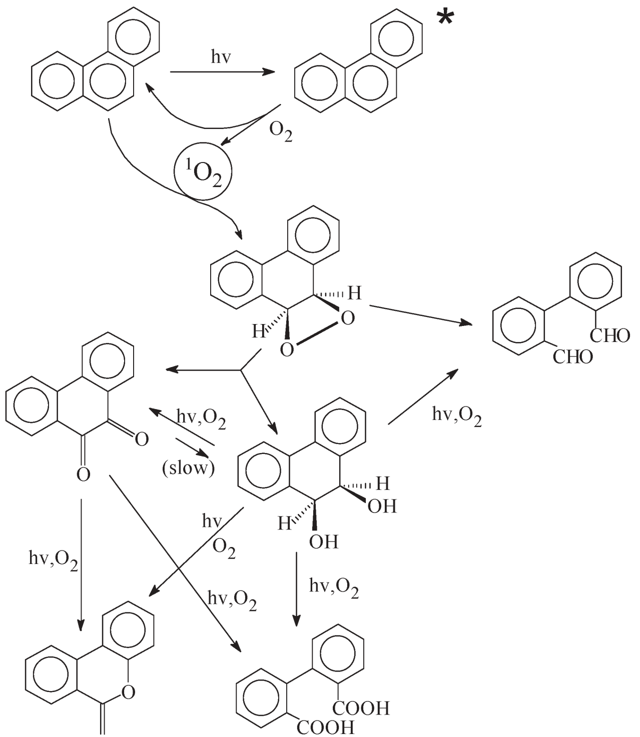
3. Direct photolysis processes

Direct photolysis (see reactions 1–3) can be important both because it induces transformation of a certain compound, and because the photolysis products can exhibit significant reactivity. For instance, direct photolysis of H_2O_2, NO_3^-, NO_2^-, HNO_2 and $FeOH^{2+}$ is a source of hydroxyl in the atmospheric aqueous phase.[8] However, this section will deal with the direct photolysis processes responsible for the transformation of the primary compounds. The rate of direct photolysis strongly depends on the nature of the substrate, and in the case of many photolabile compounds this process is likely to dominate the transformation kinetics. Direct photolysis can take place both on particulate matter and inside droplets. In the case of many organic compounds, and of PAHs in particular, more is known about their reactions on particulate matter.[9–12] Direct photoreactions on particles might however be more significant than those occurring inside droplets because particles usually exhibit longer atmospheric lifetimes.

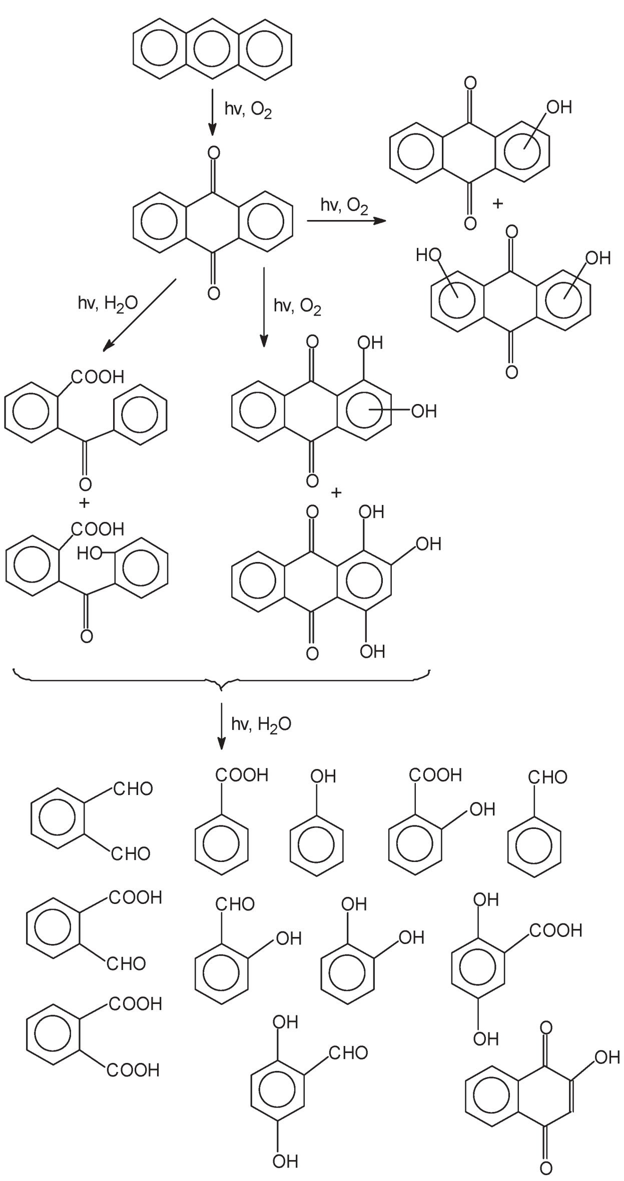
Many studies have been performed regarding the direct photolysis of Polycyclic Aromatic Hydrocarbons (PAHs) on real or simulated particulate matter. The interest in these compounds is motivated by their mutagenicity and carcinogenicity. However, many of the findings are of general applicability to all the compounds, absorbing solar radiation, which are present on atmospheric particulate matter.

The wide electron delocalisation in PAH molecules allows them to absorb sunlight. Irradiation in the absence of oxygen mainly results in photodimerisation, while irradiation under atmospheric conditions leads to photooxidation. Fairly complete photooxidation pathways have been proposed for phenanthrene[9] and pyrene[10] adsorbed on silica, and for anthracene[11] in aqueous solution (Schemes 2–4). The reaction between light-excited phenanthrene and oxygen (see Scheme 2) is thought to initially involve an excited triplet state of phenanthrene and ground-state oxygen, with generation of singlet oxygen. The latter is then added to ground-state phenanthrene.[9] In the case of anthracene photodegradation (Scheme 3), although many mechanistic details are still to be elucidated, most notable is the formation of 9,10-anthraquinone in the first step of the reaction. 9,10-Anthraquinone is in fact a powerful photosensitiser, able to induce photodegradation of many organic compounds (see Section 4).[11]

An assessment of the photochemical behaviour of many PAHs, adsorbed on silica gel, has been carried out under comparable irradiation conditions (simulated sunlight, 17.6 W m^{-2} irradiance).[5] Fast photodegradation was observed for benz[*a*]anthracene, perylene, anthracene and benz[*a*]pyrene (half life lower than 5 hours), while for instance pyrene ($\sim$20 h), benz[*e*]pyrene (70 h), crysene (100 h) and phenanthrene (150 h) showed much lower photoreactivity. It can therefore be assumed that benz[*a*]anthracene, perylene, anthracene, and benz[*a*]pyrene are likely to undergo direct photolysis as a very important transformation process in the particulate phase. The photolysis rate is higher for those molecules with lower abstraction energies for their π electrons.[5] Indeed, a correlation has been found between the Dewar reactivity numbers (abstraction energies for the π electrons, expressed in terms of the molecular orbital resonance integrals) and the observed half-life times. It was found a life-time increase of about 27 hours for an increase of 0.1 units of the Dewar reactivity number. This finding sounds reasonable when considering that, for instance, pyrene photooxidation is initiated by either electron abstraction by molecular oxygen on light-excited pyrene, or by pyrene photoionisation (see Scheme 4).[10] The main difference between the two observed pathways of pyrene photolysis, both involving electron abstraction, is that electron transfer from excited pyrene to oxygen would be energetically favoured over photoionisation as far as the isolated molecule is concerned, while pyrene adsorption on silica would make the oxygen-independent photoionisation a competitive reaction pathway.[10]

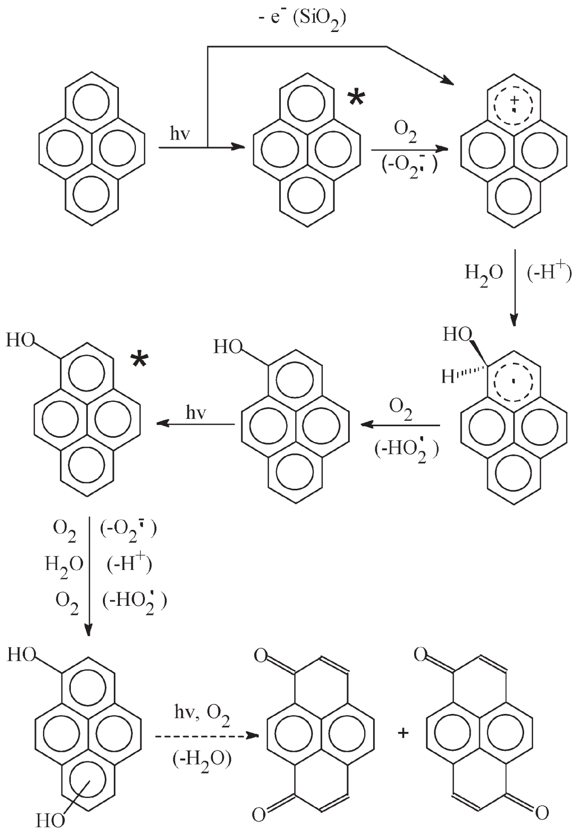


Scheme 2 Proposed direct photolysis pathways of phenanthrene adsorbed on silica gel, in the presence of oxygen.



Scheme 3 Proposed direct photolysis pathways of anthracene in aerated aqueous solution.

Molecular structure is however not the single most important parameter in defining PAH photooxidation rates on particles. Many studies indicate that PAH half-lives greatly vary depending on the substrate on which they are adsorbed.[12] Carbonaceous material was shown to strongly protect PAHs from photodegradation, which was much faster on the mineral fraction of particulate matter (mainly made up of oxides, carbonates, and silicates). The role of the magnetic fraction (iron oxides) was somewhat controversial: some authors found a slight protection effect on photodegradation, while others did not. The main factor to account for the observed differences between the various particulate components is their colour: carbonaceous material is black or otherwise very dark and can absorb a substantial fraction of light, thus protecting PAHs from photodegradation. On the other hand, degradation is faster on the lighter-shaded mineral components. The controversial role of iron oxides can be tentatively



Scheme 4 Proposed direct photolysis pathways of pyrene adsorbed on silica gel, in the presence of oxygen.

accounted for as follows: on one hand they absorb sunlight (their colour varies from orange-yellow to dark red) and can act as shields against PAH photodegradation, on the other hand irradiated iron oxides can induce transformation reactions on their own, with degradation of organic compounds (see also Section 7).[13] It is interesting to observe that the fastest PAH degradation takes place on solids that are white in colour (although of limited environmental significance) such as pure silica and alumina, which afford the least absorption of radiation.[12]

While most of these studies have been carried out on PAHs as substrates, the colour of the particulate matter influences the intensity of incident radiation available for any adsorbed molecule. Therefore this effect is considered to be a feature of the particulate matter itself and would affect the rate of photolysis of any adsorbed substrate. In the case of PAHs, in spite of the importance of photolysis as a transformation process on particulate matter, the ability of carbonaceous particles to shield radiation would make direct photolysis on fine particles slower than the reactions with active species in the gas phase (mainly $^{\bullet}$OH and $^{\bullet}$NO$_3$, O$_3$ to a far lesser extent and limited to particular cases such as acenaphthylene). Furthermore, the organic loading of the particles can inhibit the reactions between these reactive species and the adsorbed compounds in the particulate phase. Accordingly, high-molecular weight PAHs (5 rings or higher), mainly associated with particulate matter, have higher atmospheric lifetimes than more volatile PAHs of lower molecular weight.[14]

An additional photodegradation scenario for high-molecular weight PAHs can also be envisaged. PAHs associated with protective carbonaceous particles are in equilibrium with the gas phase, depending on their volatility. Accordingly, PAH transfer from carbonaceous to mineral particulate matter can take place. Depending on PAH volatility, photodegradation on mineral particles might be more important than the reactions taking place in the limited time spent in the gas phase.

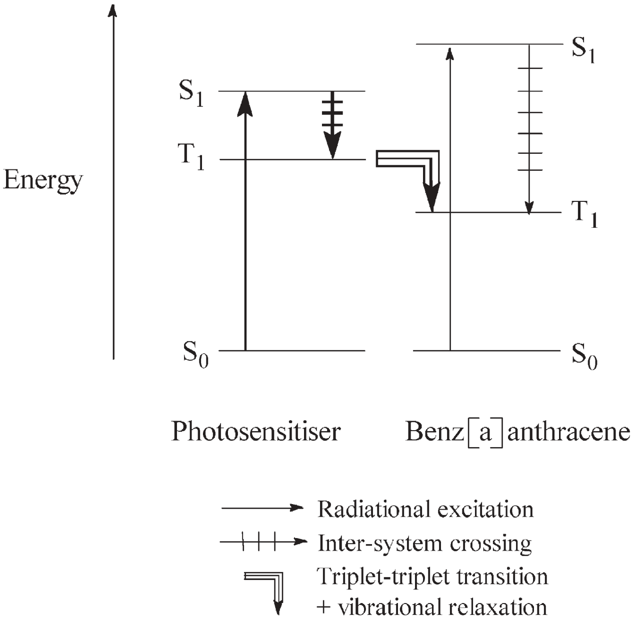
It is interesting to observe that PAH photolysis on particulate matter under atmospheric conditions, while being a removal process for the parent compounds, is a source of oxygenated aromatics (see Schemes 2–4), some of which are toxic and/or mutagenic. Furthermore, oxygenated aromatic compounds such as anthraquinones and aromatic carbonyls, which are generated upon PAH oxidation as well as directly emitted by combustion processes, are well known photosensitisers (see the Section 4 below). Moreover PAHs, during their sometimes long residence on particulate matter, are exposed to reactive species such as the nitrating agents HNO$_3$, $^{\bullet}$NO$_2$/N$_2$O$_4$, and possibly peroxynitrous acid, HOONO. Accordingly, reactions on particulate matter are potential sources of strongly mutagenic nitro-PAHs.[14]

4. Photosensitised reactions

Many transformation processes in the atmosphere are initiated by the interaction between molecules after the absorption of radiation, rather than by direct photolysis. Sensitised photolysis is known to be a significant pathway for the transformation of organic compounds in natural waters and, although a larger amount of data is available for surface waters than for atmospheric aerosols, it can be hypothesised with reasonable confidence that photosensitised processes also play an important role in the phototransformation of organic compounds on particles and inside droplets. Atmospheric aerosols contain in fact a significant amount of photosensitisers, such as quinones and aromatic carbonyls, which are also products of PAH photolysis (Schemes 2–4).[15,16] Sensitised photolysis would be particularly important for those compounds that undergo negligible or limited direct photolysis.[5,15,16]

A photosensitised process requires radiation absorption by the photosensitiser, followed by chemical reaction or energy transfer between the excited photosensitiser and other molecules. The latter undergo transformation, while the photosensitiser does not necessarily degrade in the process: sometimes the reaction pathways are able to restore the original sensitiser molecule, in which case the process is photocatalytic.

The potential for atmospheric aerosols to induce the phototransformation of organic molecules has been assessed in a comprehensive study, where many different compounds known to be present on particulate matter have been tested as potential photosensitisers.[15,16] Benz[*a*]anthracene was used as a substrate, and some quinones, aromatic carbonyls and furans were found to be active photochemical sensitisers. This means that photodegradation of benz[*a*]anthracene in the presence of the photosensitiser is considerably faster than the photodegradation of benz[*a*]anthracene alone. For this phenomenon to occur, two conditions have to be achieved. The first is that the formation rate of the excited photosensitiser must be faster than the formation rate of excited benz[*a*]anthracene, otherwise radiation absorption by benz[*a*]anthracene, and possibly its direct photolysis, would be favoured. For this to occur, the energy difference between the ground-state and the first excited singlet state of the photosensitiser must be lower than the corresponding difference for benz[*a*]anthracene. Secondly, the excited photosensitiser must be able to transfer energy to ground-state benz[*a*]anthracene, yielding excited benz[*a*]anthracene. This means that the difference between the first triplet state and the ground state of the photosensitiser must be higher than the corresponding difference for benz[*a*]anthracene. The energy transfer then occurs between the triplet states of the photosensitiser and benz[*a*]anthracene (see Scheme 5).



Scheme 5 Radiation absorption and energy transfer processes involved in sensitised photolysis. The arrows in bold indicate the main processes. The excited vibrational levels of each electronic energy state, and the corresponding processes of vibrational relaxation to the ground state (see Scheme 1), have been omitted for sake of brevity.

To explain this phenomenon mechanistically, let BaA be benz[*a*]anthracene and S the sensitiser. The following reactions can occur upon irradiation:

$$\mathrm{BaA} + h\nu \rightarrow \mathrm{BaA}^* \tag{6}$$

$$\mathrm{S} + h\nu \rightarrow \mathrm{S}^* \tag{7}$$

$$\mathrm{S}^* + \mathrm{BaA} \rightarrow \mathrm{S} + \mathrm{BaA}^* \tag{8}$$

$$\mathrm{BaA}^* \rightarrow \mathrm{Products} \tag{9}$$

For S to act as an efficient photosensitiser, reaction 7 must be faster than reaction 6, and reaction 8 must be thermodynamically allowed. Clearly, such conditions are valid for any substrate other than benz[*a*]anthracene.[15] For instance, similar reactions have been described for 1-nitropyrene and 3-nitrofluoranthene as substrates in the presence of anthraquinone as sensitiser.[17]

Photosensitised degradation of organic compounds in the presence of quinones and aromatic carbonyls is also an important source of hydrogen peroxide in atmospheric aerosols.[18] Hydrogen peroxide is then involved in various processes, including most notably the oxidation of S(IV) to sulfuric acid.[3] The following reactions account for H_2O_2 production (with S as the photosensitiser and R–H as the substrate):

$$\mathrm{S}^* + \mathrm{R{-}H} \rightarrow \mathrm{S{-}H}^{\bullet} + \mathrm{R}^{\bullet} \tag{10}$$

$$\mathrm{S{-}H}^{\bullet} + \mathrm{O_2} \rightarrow \mathrm{S} + \mathrm{HO_2}^{\bullet} \tag{11}$$

$$2\,\mathrm{HO_2}^{\bullet} \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \tag{12}$$

$$\mathrm{R}^{\bullet} \rightarrow \mathrm{Products} \tag{13}$$

In some cases the excited sensitiser molecule, S*, exclusively undergoes reactions 10,11. In this way the initial molecule S is restored and no depletion of S will be observed, while R–H degrades and H_2O_2 is formed. This is the case when 3,4-dimethoxybenzaldehyde (S) is irradiated in the presence of phenol (R–H, see Scheme 6).[18]

The scenario described above is not always observed. Under comparable conditions, the sensitisers 2- and 3-methoxybenzaldehyde undergo degradation together with the substrate (phenol).[18] A possible explanation is a reaction between S* and S, where ground-state S behaves as a substrate, which results in S transformation (see Scheme 6). Consistently with this hypothesis, irradiation of 9,10-anthraquinone alone in solution yields H_2O_2 and induces anthraquinone degradation. In such a case the same compound acts both as sensitiser upon radiation absorption and as substrate.[19]

A second possibility to explain the degradation of S is that the reduced sensitiser, S–H$^{\bullet}$, undergoes further transformation processes that compete with reaction 11. This behaviour has been observed in the presence of methoxyphenols as substrates, which enhance the photodegradation of various aromatic compounds such as PAHs and nitro-PAHs.[20] Methoxyphenols are not able to act as sensitisers in such systems: they are PAHs and nitro-PAHs that absorb radiation and behave like S. As oxidisable substrates, methoxyphenols can reduce light-excited PAHs and nitro-PAHs. The photodegradation of the latter would occur because hydrogenated PAHs and nitro-PAHs (S–H$^{\bullet}$) would not regenerate the starting compound on reaction 11 with oxygen, but would be involved in further transformation processes.[20]

The atmospheric impact of the photochemical transformations enhanced by methoxyphenols is potentially very significant because these compounds are major components of wood smoke aerosol.[20] It would therefore be very important to determine if the described process is peculiar to PAHs and nitro-PAHs as sensitisers, or if it represents a more general phenomenon induced by methoxyphenols as substrates. Anyway, methoxyphenol-enhanced photodegradation is likely to play an important role in inducing transformation of particle-adsorbed PAHs and nitro-PAHs, and in particular of those compounds that undergo slow direct photolysis.

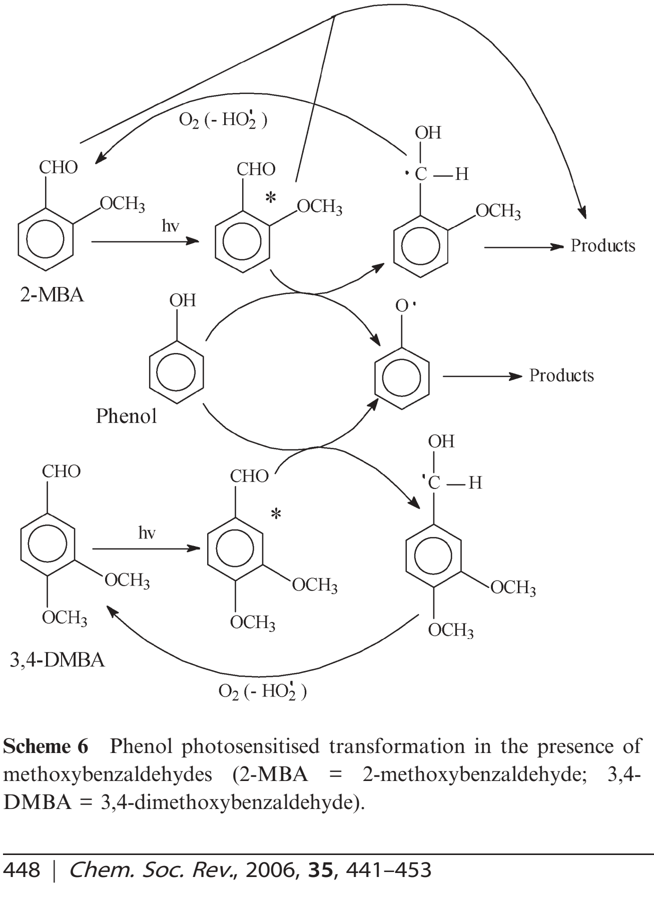
In the context of photosensitised reactions the detection, in atmospheric water, of organic material with similar features to the humic acids (Humic-Like Substances, HULIS) may be very important.[21,22] Actually, humic acids are important photosensitisers in natural waters, and HULIS might play a similar role in the atmosphere. It is clear that the photochemical properties of HULIS deserve more attention.

5. Nitrate photochemistry

Nitrate is an important component of inorganic particulate matter, where it is mainly present as NH_4NO_3 and $NaNO_3$. Aqueous nitrate is well known to undergo photolysis upon UV irradiation, yielding $^{\bullet}OH$ and $^{\bullet}NO_2$ with a quantum yield of 0.01:

$$NO_3^- + h\nu + H^+ \rightarrow {}^{\bullet}NO_2 + {}^{\bullet}OH \qquad (14)$$

The radical $^{\bullet}OH$ is a very strong oxidant ($E^\circ = 2.59$ V) and very reactive. It is therefore able to oxidise a huge number of organic and inorganic compounds, very often with high reaction rates.[7] Accordingly, the hydroxyl radical plays a very important role in atmospheric chemistry.[8]



Scheme 6 Phenol photosensitised transformation in the presence of methoxybenzaldehydes (2-MBA = 2-methoxybenzaldehyde; 3,4-DMBA = 3,4-dimethoxybenzaldehyde).

It has recently been found that irradiation of nitrate-containing ice results in the production of nitrogen dioxide, which might constitute an important source of $^{\bullet}NO_2$ in irradiated snow layers in the polar regions.[23] It has also been found that the UV irradiation of solid $NaNO_3$ yields nitrogen dioxide. Such a process also yields hydroxyl in the presence of a H^+ donor, *e.g.* water vapour.[24] The generation of $^{\bullet}OH$ and $^{\bullet}NO_2$ can induce nitration reactions in the gas phase,[1,2] and nitration of benzene vapour has been observed upon irradiation of solid $NaNO_3$.[24]

Nitrogen dioxide reacts slowly in the gas phase, where nitration processes have to be initiated by $^{\bullet}OH$ or $^{\bullet}NO_3$.[1,2] The situation is completely different for particle-adsorbed compounds. Reaction of pyrene, fluoranthene, and anthracene with $^{\bullet}NO_2$ in the presence of HNO_3 traces might account for the occurrence of 1-nitropyrene, 2-nitrofluoranthene and 9-nitroanthracene on particulate matter in the Antarctic coast.[24] The formation of aromatic nitro-derivatives on particulate matter would be very important because these compounds are powerful mutagens and suspected carcinogens, and the cited aerosol-phase processes might also occur at temperate latitudes. The different reactivity of nitrogen dioxide in the gas phase (almost unreactive) and on particles (effective nitrating agent as in aqueous solution) might perhaps be due to the involvement of the dimer N_2O_4 in nitration processes both on particles and in solution, differently from the gas phase, although many details of the N_2O_4 reactivity towards aromatic compounds under different conditions are still to be elucidated.[24–26]

Interestingly, evidence is available for the photochemical generation of peroxynitrous acid, HOONO, upon UV irradiation of solid nitrate in the presence of H^+ donors such as NH_4^+, and water molecules adsorbed on α-Fe_2O_3. HOONO is a powerful hydroxylating and nitrating agent.[24,26]

Nitrate is also present in atmospheric waters at an average concentration somewhat higher than 10^{-4} M.[8] Its importance as a photochemical hydroxyl source in a typical continental fair weather cloud is second only to the photolysis of H_2O_2.[8] Apart from being a hydroxyl source, nitrate is known to induce aromatic photonitration on UV irradiation, yielding toxic and potentially carcinogenic nitroaromatic compounds.[25,26] Nitrate irradiation in solution yields $^{\bullet}NO_2/N_2O_4$, HNO_2 and peroxynitrous acid as nitrating agents. Unlike the gas phase nitrogen dioxide is a powerful nitrating agent in solution. UV irradiation of acidic nitrate solutions also yields HNO_2 *via* various pathways (see reactions 14 to 17), which is then able to nitrate activated aromatic hydrocarbons (*e.g.* phenolic compounds, but not benzene and naphthalene) *via* a dark process.[26]

$$NO_3^- + h\nu + H^+ \rightarrow HNO_2 + O \qquad (15)$$

$$2\ {}^{\bullet}NO_2 \rightleftarrows N_2O_4 \qquad (16)$$

$$N_2O_4 + H_2O \rightarrow H^+ + NO_3^- + HNO_2 \qquad (17)$$

It has recently been found that the enhancement at acidic pH of phytotoxic nitrophenol formation on nitrate irradiation is due to a dark nitration reaction involving photoformed HNO_2.[14] Nitrate photolysis is also a potential source of HNO_2 in sunlight-irradiated polar snow and ice. HNO_2 in these environments has been found to initiate a photochemical smog process with generation of tropospheric ozone.[23]

Peroxynitrous acid, HOONO, an isomer of nitric acid (which would be indicated as $HONO_2$ in this context), forms upon nitrate photoisomerisation (reactions 18,19). It is a weak acid in aqueous solution ($pK_a \cong 7$) and a powerful nitrating agent, able for instance to nitrate phenol, benzene, and naphthalene.[26]

$$NO_3^- + h\nu \rightarrow ONOO^- \quad (18)$$

$$ONOO^- + H^+ \rightleftarrows HOONO \quad (19)$$

The occurrence of HOONO in the atmosphere is a current research topic. This compound is thought to be formed in the gas phase upon reaction between $^{\bullet}OH$ and $^{\bullet}NO_2$, in the presence of a third molecule that helps the dissipation of the excess energy (a similar process would also lead to the formation of the more stable nitric acid). Unfortunately, incomplete knowledge of the transformation processes of HOONO in the gas phase makes it difficult to evaluate the atmospheric lifetime of this compound and, as a consequence, to estimate its gas-phase concentration.[27] As far as the aqueous phase is concerned, HOONO forms upon reactions 18,19, in the presence of $HNO_2 + H_2O_2$, and of $HO_2^{\bullet} + {}^{\bullet}NO$. It is most likely a low-concentration transient, due to its very fast isomerisation to nitric acid. While in-field measurement of aqueous-phase HOONO is understandably difficult, its formation would result in oxidation/hydroxylation and nitration of aromatic compounds.[26]

In summary, nitrate photolysis contributes to the photochemical generation of hydroxyl in atmospheric waters (although to a lesser extent than the photolysis of H_2O_2), but it can be expected to play an even more important role in particulate matter, of which sodium and ammonium nitrates are major constituents. UV irradiation of ice and snow containing nitrate, and of solid nitrate in the presence of water vapour yields $^{\bullet}OH + {}^{\bullet}NO_2$ (reaction 14).[23] Such a process is likely to be a significant source of hydroxyl radicals and nitrogen dioxide in remote areas (*e.g.* the Antarctica), while its significance in mid-latitude continental areas is still to be assessed.

6. Nitrite photochemistry

Nitrite is present in atmospheric waters at an average concentration level of 10^{-7}–10^{-6} M. Under these circumstances it plays a minor role as a photochemical hydroxyl source.[8] The situation is however very different in polluted areas, where direct traffic emissions and the atmospheric oxidation of $^{\bullet}NO$ by $^{\bullet}OH$ are very important sources of gas-phase HNO_2. A further contribution, although to a lesser extent, is given by the heterogeneous conversion of $^{\bullet}NO_2$ on soot particles.[4] Under these circumstances HNO_2 can then dissolve in fog, dew and cloudwater to yield nitrite. In a study that will probably become a milestone of nitrite atmospheric photochemistry, Anastasio and McGregor detected nitrite at concentration values approaching 10^{-4} M in fogwater from California's Central Valley.[28] Irradiation of fogwater samples indicated that nitrite photolysis accounted for 50–100% of hydroxyl photoformation.[28] The UV photolysis of nitrite yields $^{\bullet}OH$ with a quantum yield of 0.025 at 360 nm. Hydroxyl can further oxidise NO_2^- to $^{\bullet}NO_2$:

$$NO_2^- + h\nu + H^+ \rightarrow {}^{\bullet}NO + {}^{\bullet}OH \quad (20)$$

$$NO_2^- + {}^{\bullet}OH \rightarrow {}^{\bullet}NO_2 + OH^- \quad (21)$$

On irradiation of the cited fogwater samples, the rate of $^{\bullet}OH$ photogeneration was comparable to the typical mass-transfer rate of gaseous $^{\bullet}OH$ to the liquid phase, and might be significantly higher for larger droplets (diameter > 20 μm), for which mass-transfer is less efficient.[28] This is very interesting because, when considering cloudwater in remote areas, $^{\bullet}OH$ transfer from the gas phase is usually faster than *in situ* photochemical generation.[8] The steady-state $[^{\bullet}OH]$ found by Anastasio and McGregor upon irradiation of their samples was such as to induce degradation of a compound reacting with hydroxyl at a diffusion-controlled rate (second order rate constant around 10^{10} M^{-1} s^{-1}) on a time scale of 20–40 h under winter-time conditions. Under summer-time conditions the time scales would be reduced by a factor of 2.[28]

As to the importance of reaction 21, yielding $^{\bullet}NO_2$, the cited authors found that nitrite accounted for 10–30% of hydroxyl scavenging.[28] Under such circumstances significant generation of nitrogen dioxide can be expected to take place. Nitrite/nitrous acid were also found to be important photochemical sources and scavengers of hydroxyl radicals in dew water, which is particularly rich of NO_2^-/HNO_2.[29]

Irradiation of fogwater spiked with amino compounds mainly yielded oxidised intermediates, most likely resulting from the reaction between the substrates and hydroxyl. A small amount of a nitroso-derivative was also detected.[30] Various studies have shown that amine nitrosation, with formation of carcinogenic nitrosamines, can be initiated by HNO_2, N_2O_3, and $^{\bullet}NO_2 + {}^{\bullet}NO$.[31] N_2O_3, $^{\bullet}NO_2$, and $^{\bullet}NO$ are formed upon nitrite photolysis (N_2O_3 upon reaction between $^{\bullet}NO$ and $^{\bullet}NO_2$), and nitrosation of dimethylamine has for instance been observed in the presence of nitrite under irradiation.[32] Nitrite under irradiation is also able to nitrate various aromatic hydrocarbons.[32] Interestingly, oxidation of nitrite to nitrogen dioxide can take place in the presence of various sources of hydroxyl and other oxidising species. Nitrate, metal oxides, and dissolved Fe(III), all under irradiation, and Fenton and photo-Fenton systems can all interact with nitrite to yield nitrogen dioxide, therefore enhancing aromatic nitration.[33,34] Nitration processes in the atmospheric aqueous phase (dark or photoinduced) might be significant: field data have shown that the atmospheric formation of the powerful phytotoxic agent 2,4-dinitrophenol is closely connected with the presence of cloud events, while it is negligible under fair weather conditions when water droplets are not available.[33]

The case of nitrite photochemistry is interesting because, while playing a secondary role on an average continental scale,[8] it can be the main (and in some cases the almost exclusive) photochemical source of hydroxyl in the aqueous phase in polluted areas.[28–30] Furthermore, the instability of nitrite in atmospheric waters (the reaction of HNO_2 with H_2O_2 at acidic pH is for instance very fast),[34] while limiting $[NO_2^-]$ in such compartments, also makes analytical artefacts very likely as nitrite can easily undergo further transformation in the time interval between sampling and analysis. It this therefore possible for the nitrite concentration in atmospheric water samples to be underestimated due to oxidation to nitrate after sampling. As a result it is not possible to exclude that the role of nitrite photochemistry in atmospheric water droplets has also been underestimated.

7. Photochemistry of Fe(III) species and hydrogen peroxide

Fe(III) species play an important role in the photochemistry of the atmospheric aerosol phase, both in droplets (dissolved Fe(III)) and on particles (ferric oxides). Fe(III) compounds are able to produce reactive species upon irradiation. When focusing upon ${}^{\bullet}OH$ photoproduction, the most photoactive compound is $FeOH^{2+}$ with a quantum yield of 0.2 at 300 nm:[32]

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \tag{22}$$

With respect to the atmospheric aqueous phase, the photolysis of $FeOH^{2+}$ contributes to the photochemical generation of hydroxyl radicals to a lesser extent than H_2O_2 and NO_3^-.[8] $FeOH^{2+}$ is the prevailing monomeric Fe(III) species at $3 < pH < 5$. In natural waters, dimeric and polymeric Fe(III) compounds are also present. Irradiation of these species has little effect in yielding ${}^{\bullet}OH$, but it is likely to induce charge-transfer reactions, which are able to transform some dissolved molecules.[32–36]

Around neutral pH iron oxide colloids are the most stable Fe(III) form, and they are photoactive as well. UV irradiation of the Fe^{III}–OH surface groups of the oxides yields $Fe^{2+} + {}^{\bullet}OH$ in a similar way to reaction 22, while irradiation in the visible region induces charge-transfer processes upon generation of electron/hole couples (e^-/h^+, see Scheme 7). The latter processes are able to induce redox transformation of compounds adsorbed onto the oxide surface as surface complexes. Accordingly, oxidation of oxalate to CO_2 and of S(IV) to sulfate upon irradiation of hematite (α-Fe_2O_3) has been observed.[13] Charge-transfer processes are more selective than ${}^{\bullet}OH$ reactions towards substrate transformation. For instance, visible-light irradiation of α-Fe_2O_3 and β-FeOOH induces phenol transformation at a very low rate, while nitrite is readily oxidised to nitrogen dioxide. The latter is then able to nitrate phenol, and relevant phenol transformation to nitrophenols is thus observed upon iron oxide irradiation in the presence of nitrite (see also Scheme 8).[33] Interaction between hematite (α-Fe_2O_3) and solid nitrate also results in enhanced aromatic nitration, possibly *via* formation of HOONO.[24]

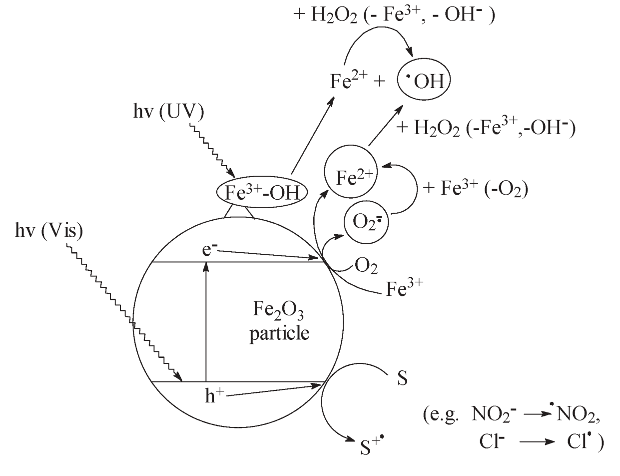
The generation of Fe(II) in reaction 22 (and similar processes upon UV irradiation of iron oxides) is also interesting because ferrous ions can react with H_2O_2 in the Fenton reaction. Hydrogen peroxide, present in the atmospheric aqueous phase at concentration levels in the range 10^{-6}–10^{-4} M, is also an important photochemical source of hydroxyl on its own (for reaction 23, a quantum yield of about 0.50 has been reported).[8] Moreover, the Fenton reaction 24 between Fe(II) and H_2O_2 yields further hydroxyl radicals (see also Scheme 7).[13]

$$H_2O_2 + h\nu \rightarrow 2\ {}^{\bullet}OH \tag{23}$$

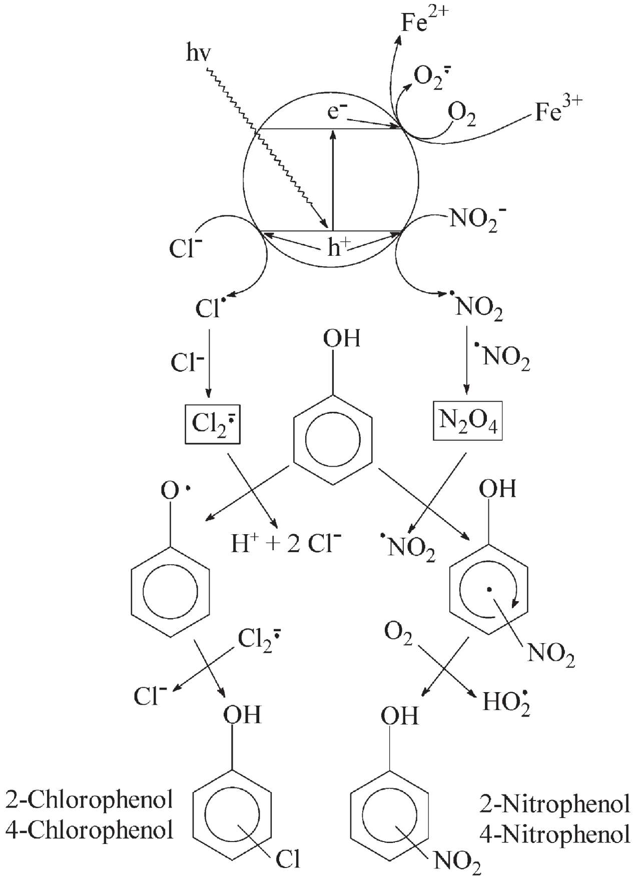
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \tag{24}$$

It should be noted that $FeOH^{2+}$ photolysis is not the only source of Fe(II) in cloudwater. Fe(III) reduction can take place upon reaction with Cu(I), $HO_2^{\bullet}/O_2^{-\bullet}$, HSO_3^-, and H_2O_2. Reaction with Cu(I) is likely to be the main process of Fe(III) reduction under most conditions, while Cu(I) mainly forms upon Cu(II) reduction by $HO_2^{\bullet}/O_2^{-\bullet}$. The latter derive from many reactions: $O_3 + {}^{\bullet}OH$, $H_2O_2 + {}^{\bullet}OH$, radicals $R^{\bullet} + O_2$. In a typical continental fair weather cloud, in the presence of 10^{-6} M iron, reaction 24 can account for up to one half of ${}^{\bullet}OH$ generation.[8]

Finally it is interesting to observe that irradiated Fe(III) species (both dissolved Fe(III) and iron oxides) can oxidise chloride ions to the corresponding $Cl^{\bullet}$ radicals. In the presence of chloride, $Cl^{\bullet}$ would further react to yield $Cl_2^{\bullet-}$. The species $Cl^{\bullet}/Cl_2^{\bullet-}$ can be involved in the chlorination of organic compounds (*e.g.* phenol to chlorophenols and chloroform to tetrachloromethane).[37] In the case of dissolved Fe(III), the most active species in the production of $Cl^{\bullet}/Cl_2^{\bullet-}$ is $FeOH^{2+}$, which yields ${}^{\bullet}OH$ upon photolysis (reaction 22). Hydroxyl is then able to produce $Cl^{\bullet}/Cl_2^{\bullet-}$ upon oxidation of chloride in acidic solution (reactions 25–27). Also Fe^{3+} is a hydroxyl source, although much less active than $FeOH^{2+}$.[32,35] Direct $Cl^{\bullet}$ photogeneration can even take place upon photolysis of



Scheme 7 Photochemical reaction induced by irradiation of Fe(III) oxides in aerated aqueous solution. h^+ = valence-band hole; e^- = conduction-band electron.



Scheme 8 Photochemical formation of aromatic nitro- and chloro-derivatives upon irradiation of ferric oxides in the presence of nitrite and chloride ions. h^+ = valence-band hole; e^- = conduction-band electron.

$FeCl^{2+}$ (reaction 28), but such a process is less effective than that initiated by $FeOH^{2+}$ photolysis.[37]

$$Cl^- + {}^{\bullet}OH \rightleftarrows ClOH^{-\bullet} \qquad (25)$$

$$ClOH^{-\bullet} + H^+ \rightleftarrows Cl^{\bullet} + H_2O \qquad (26)$$

$$Cl^{\bullet} + Cl^- \rightleftarrows Cl_2^{\bullet -} \qquad (27)$$

$$FeCl^{2+} + h\nu \rightarrow Fe^{2+} + Cl^{\bullet} \qquad (28)$$

The corresponding chlorination processes initiated by irradiation of iron oxides are reported in Scheme 8.[37] An important difference between the nitration and the chlorination of phenol is that the former is thought to take place upon ring addition followed by hydrogen abstraction,[24] while chlorination is likely to proceed *via* hydrogen abstraction to give phenoxyl, followed by reaction between phenoxyl and a chlorine radical.[37] The discriminating feature of the two processes is the effect of oxygen. O_2 being required in the final step of the nitration process (hydrogen atom abstraction from the radical intermediate), nitrophenol formation is favoured in oxygenated solution.[24] By contrast, O_2 does not take part in the chlorination of phenol. Furthermore, as oxygen does not scavenge the chlorination intermediates phenoxy radicals at a significant extent, no effect of dissolved oxygen on phenol chlorination has been observed.[37] However, it should be noted that dissolved oxygen is required as scavenger of conduction-band electrons (e^-) in the presence of illuminated Fe(III) oxides. In the absence of oxygen, the excess of e^- would considerably inhibit the oxidation reactions of NO_2^- to $^{\bullet}NO_2/N_2O_4$ and of Cl^- to $Cl^{\bullet}/Cl_2^{-\bullet}$. It follows that iron oxides might not be suitable systems for mechanistic studies of phenol nitration and chlorination. Actually, the reaction pathways reported in Scheme 8 have been elucidated in homogeneous systems (nitrite photolysis for nitration,[24] photolysis of dissolved Fe(III) in the presence of Cl^- for chlorination[37]).

In summary, the photochemical processes initiated by iron oxides and dissolved Fe(III) can be involved in acid rain (as far as the oxidation of S(IV) to S(VI) is concerned), aromatic nitration, and organohalogen formation.

8. Conclusions

Important photochemical reactions of atmospheric significance can take place on the surface of particulate matter and inside water droplets (*e.g.* mist, fog, dew, clouds). Direct and sensitised photolysis processes, though more studied for particles, can take place in both environments. When considering photochemical reactions occurring on atmospheric particulate matter, it is observed that the atmospheric lifetime of particles is often longer when compared with water droplets, which results in longer times for the processes to take place. This would compensate the often slower reaction rates that are observed on particles when compared to water droplets.[5,8]

As far as the most studied class of compounds (PAHs) is concerned, direct photolysis/photooxidation on particles can be an important transformation process for readily photolysed molecules (*e.g.* anthracene, benz[*a*]anthracene, perylene, benz[*a*]pyrene). In spite of this, the radiation screening operated by carbonaceous particles, together with the poorly efficient gas-to-particle mass transfer of reactive radical species (*e.g.* $^{\bullet}OH$, $^{\bullet}NO_3$), imply that transformation processes on particulate matter would be relatively slow. Accordingly, molecules adsorbed on particulate matter would often undergo slower degradation, resulting in longer atmospheric lifetimes, when compared to those in the gas phase.

Sensitised photolysis processes can be initiated by compounds such as quinones and aromatic carbonyls, partially derived from PAH photooxidation. Sensitised transformation can be more important than direct photolysis for those compounds that are slowly photodegraded. Sensitised photolysis usually involves two molecules, of which one (the sensitiser) absorbs radiation and reacts *via* energy, electron or atom transfer with the other (the substrate). The substrate is usually degraded in the process, while in some cases the original sensitiser molecule is restored and very limited sensitiser degradation is observed. However, there are many exceptions to that behaviour and the sensitiser can undergo degradation as well. Most important in this context is the degradation of PAHs and nitro-PAHs as photosensitisers in the presence of methoxyphenols as substrates. Such a process, leading to faster degradation of PAHs and nitro-PAHs when compared with direct photolysis, is a potentially important photochemical sink of the two classes of polycyclic aromatic compounds in the atmosphere.

Nitrate, nitrite, Fe(III), and hydrogen peroxide are important photochemical sources of reactive species in atmospheric water droplets and on particulate matter. They are involved in hydroxyl photogeneration as well as other important processes (S(IV) oxidation, and nitration, nitrosation, and chlorination of organic compounds). The photolysis of NO_2^-, H_2O_2, and dissolved Fe(III) is likely to play a more important role inside water droplets, while the processes photoinduced by iron oxides and possibly nitrate should play a more important role on particulate matter.

It is interesting to discuss the role of aqueous (photo)-chemistry in the hydroxyl radical-mediated transformation of organic compounds. In a typical continental fair weather cloud the steady-state [$^{\bullet}$OH] might be around 2.5–5 × 10^{-14} M, which in the case of a compound reacting with hydroxyl at the diffusion limit (rate constant around 10^{10} M^{-1} s^{-1}) would result in a lifetime of 30–60 min.[8] Purely photochemical processes would account for about 10–15% of hydroxyl photoformation, the remainder being attributable to dark processes (mainly reaction between O_3 and $O_2^{-\bullet}$ and the Fenton reaction, together accounting for 50–80% of the total, depending on iron concentration), and to $^{\bullet}$OH transfer from the gas phase (accounting for 15–20% of total hydroxyl).[8,28] It should also be noted that some dark processes of hydroxyl formation involve transients (*e.g.* $HO_2^{\bullet}/O_2^{-\bullet}$), the generation of which is influenced by photochemical reactions.[8]

The kinetics of some gas-phase and aqueous-phase transformation processes involving $^{\bullet}$OH is reported in Table 1 in the form of atmospheric lifetimes. In the case of a compound S undergoing reaction with hydroxyl, in either phase, with pseudo-first order kinetics, it is $[S]_t = [S]_0 \exp(-k [^{\bullet}OH]\, t)$, with $[S]_t$ = concentration of S at time t, $[S]_0$ = initial concentration, [$^{\bullet}$OH] = steady-state hydroxyl concentration, and k = second-order reaction rate constant between $^{\bullet}$OH and S. In such a case the atmospheric lifetime of S would be $(k\,[^{\bullet}OH])^{-1}$, that is the time required to lower [S] by a ∼2.72 exponential factor. Table 1 also reports the corresponding lifetimes for reaction with $^{\bullet}NO_3$, an important reactive species during the night both in the gas phase[1] and in aqueous solution.[38] The occurrence of $^{\bullet}NO_3$ in atmospheric waters would mainly be accounted for by mass transfer from the gas phase.[38] The concentration values of $^{\bullet}$OH and $^{\bullet}NO_3$ in either phase, reported in Table 1, represent daily averages, so that the reported lifetimes are referred to calendar days.[8,33,38] Note that $^{\bullet}$OH is more concentrated during the day, with sharper differences in the gas phase where no hydroxyl occurs during the night. In aqueous solution the dark processes would yield some hydroxyl also during night-time. By contrast, $^{\bullet}NO_3$ is present in either phase only during the night, because of its very fast photolysis upon sunlight absorption.[1,38] 2-Propanol and phenol were considered as model substrates due to their water solubility and to the availability of the rate constants for reaction with $^{\bullet}$OH and $^{\bullet}NO_3$ in the gas phase and in aqueous solution.[1,7,38,39] Furthermore, neither substrate absorbs sunlight and they are therefore not expected to undergo direct photolysis. The lifetime data reported in Table 1 show that the atmospheric degradation of 2-propanol would occur upon reaction with $^{\bullet}$OH rather than $^{\bullet}NO_3$, and that the hydroxyl-initiated process is seven times faster in solution than in the gas phase. A similar phase ratio for hydroxyl-initiated degradation kinetics is observed for phenol, which however also undergoes fast reaction with $^{\bullet}NO_3$. Given the atmospheric occurrence of the two radical species it can be hypothesised that phenol degradation can take place upon reaction with hydroxyl (faster in solution) during the day, and upon reaction with $^{\bullet}NO_3$ (faster in the gas phase) during the night.

Table 1

		Atmospheric lifetimes[b]	
		2-Propanol	Phenol
$^{\bullet}$OH	Gas phase[a] (10^6 molecules cm^{-3})	2 days	10 hours
	Aqueous phase[a] (2 × 10^{-14} M)	7 hours	1 hour
$^{\bullet}NO_3$	Gas phase[a] (2 × 10^8 molecules cm^{-3})	>25 days	20 minutes
	Aqueous phase[a] (10^{-13} M)	>45 days	1.5 hours

[a] For gas-phase concentrations see Ref. 33. For the aqueous-phase values, see Ref. 8 for $^{\bullet}$OH and Ref. 38 for $^{\bullet}NO_3$. [b] Time needed to decrease the initial concentration of the substrate (2-propanol, phenol) by an exponential factor, calculated as $(k\,[\mathrm{Radical}])^{-1}$. The adopted second-order rate constants k in the gas phase were 5.32 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} for 2-propanol and $^{\bullet}$OH,[1] 2.63 × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for phenol and $^{\bullet}$OH,[1] <2.3 × 10^{-15} cm^3 $molecule^{-1}$ s^{-1} for 2-propanol and $^{\bullet}NO_3$,[1] and 3.78 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} for phenol and $^{\bullet}NO_3$.[1] The adopted second-order rate constants in solution were 1.9 × 10^9 M^{-1} s^{-1} for 2-propanol and $^{\bullet}$OH,[7] 1.4 × 10^{10} M^{-1} s^{-1} for phenol and $^{\bullet}$OH,[7] 2.5 × 10^6 M^{-1} s^{-1} for 2-propanol and $^{\bullet}NO_3$,[39] and 1.8 × 10^9 M^{-1} s^{-1} for phenol and $^{\bullet}NO_3$.[38]

The role of aqueous hydroxyl chemistry as a sink for atmospheric components would obviously be linked with the gas-to-droplet partitioning rates and equilibria, and with the reactivity in the two phases. Table 1 suggests that transformation in aqueous solution would be a major sink for many hydrophilic compounds that undergo fast reaction with aqueous $^{\bullet}$OH (and/or $^{\bullet}NO_3$).[7,36]

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