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Professional paper

PHOTOCHEMICAL ACTIVATION OF AIR POLLUTANTS, RELATED TO THE PRESERVATION OF CULTURAL HERITAGE

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Abstract

It is well known that the exposition to air and weather markedly enhances derogation of all artifacts. In this report, the contribution of light (particularly sunlight) to marked speed-up of the oxidation and other changes by exposition to atmosphere will be analyzed. Five major mechanisms of the effect of insolation can be identified:

1. First is a trivial one – the heating effect which enhances all chemical processes. 2. Photoexcitation of material from which the item is made, turning it more reactive toward air oxygen (and to other present substances). 3. Sensitization of oxygen by excitation to singlet state in which it is extremely reactive, and can react even with inert materials. 4. Photochemical transformation of volatile organic compounds (VOC), primarily aldehydes and ketones, that can with oxygen yield organic acids and hydroperoxides which definitely harm majority of materials. 5. In contact of oxygen and another material, upon the absorption of light quanta, a charge transfer process can occur, giving yield to pairs of ion-radicals, which further can be transformed in various reactive products.

Key words: *Photooxygenation, Chemical mechanisms, Air pollutants.*

1. INTRODUCTION

Derogation of all items exposed to atmospheric condition is a well known fact. Under ‘atmospheric conditions’ we understand a number of particular influences: Outside temperature, availability of molecular oxygen, moisture, air pollutants, etc. One least systematically studied effect is the insolation. Insolation is the extent of the exposition to the sunlight. And can affect the essentially all materials in, at least five, different mechanistic paths. Every mechanism has variants specific for particular substances, or combination of substances. Here we shall discuss five different mechanisms for interference of sunlight with various materials.

2. DISCUSSION

Effect of heating (1). This is a trivial one, because heat always accelerates the chemical reaction. This aspect will not be further discussed here, 2 and 3 Photoexcitation of target molecules. Presence of aromatic ring and double bonds, particularly polar double bonds (>C=O , >C=N- , -N=O ; etc., so called chromophores) in molecule is the basis for efficient absorption of light quanta in visible and near-ultra violet range. Energies of these quanta match the energy of the majority of chemical bonds. Absorption of light quantum promotes the molecule in the excited state. In essence, one electron from filled orbital is promoted in one empty antibonding molecular orbital. Formerly paired electrons are now two single electrons, which can be in singlet (antiparallel spins) or triplet (parallel spins) state.

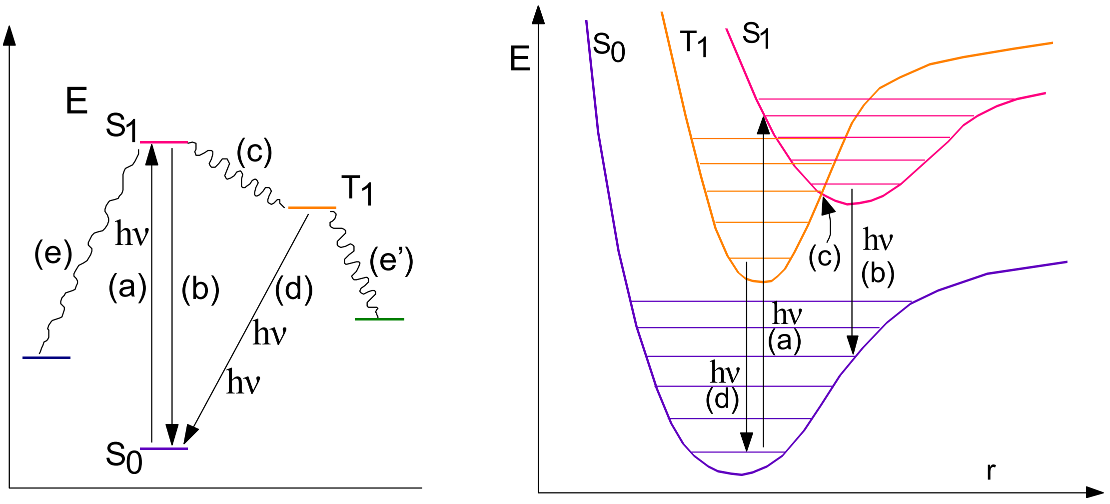


Figure 1. Schematic representation of electronic states of molecule and of related photophysical processes (right: a schematic representation of potential energy surfaces/curves; left: Jablonski diagram – a simplified representation of electronic transitions in molecules) , (a) light absorption, (b) fluorescence, (c) intersystem crossing, (d) phosphorescence, (e and e’) non-radiative relaxation (e.g. photo-chemical reaction)

An excited molecule is very rich in energy, and has several modes for the relaxation. Since almost all molecules are in singlet ground state, normally the primary photophysical process populates excited singlet state. This state has a short life-time and the major secondary process is emission of photon and the transition in ground state. Part of molecules (through the spin-orbit coupling mechanism) undergoes so called intersystem crossing, giving more stable triplet excited state. Because of the mismatch of spin states among ground and excited triplet state, this one has much longer life-time. It can decay at much slower rate and this type of photoemission is known as phosphorescence. The relative long life of triplet gives opportunity to undergo the chemical change. The most common types of chemical transformations are addition to other molecules, rearrangement, and fragmentation. All these processes yield highly reactive intermediates. Molecular oxygen, present in the air, readily reacts with photoexcited molecules, and end products are oxygenated molecular species, as hydroperoxides, acids, and other.. It's well known that such species can harm any surface in contact with them.

4 Sensitization of oxygen in excited singlet state, in which it is extremely reactive, and can react even with inert materials. As sensitizers serve the molecules which efficiently absorb the light, and easily populate triplet excited state (most common examples are: eosine, methylene blue, dicyanoanthracene, rose bengal, and other). Energy transfer between molecules which causes the change of the spin multiplicity (e.g., singlet to triplet) has very low probability (because of different symmetry of wave functions). But, the simultaneous change of the multiplicity of both molecules has no such constraint, because overall spin state of the system does not change.

$$\text{Sens}\,(S_0) \xrightarrow{h\nu} \text{Sens}\,(S_1)$$

$$\text{Sens}\,(S_1) \xrightarrow[\text{crossing}]{\text{intersystem}} \text{Sens}\,(T_1)$$

$$\text{Sens}\,(T_1) + O_2(T_1) \longrightarrow \text{Sens}\,(S_1) + O_2(S_0)$$

Many organic and coordination compounds work as triplet sensitizers. The major products of singlet oxygen are oxygenated compounds with high potential to oxidize other compounds and materials. Occasionally, these reactions can proceed without sensitizer, but the substrate itself can play that role. An interesting example is recently reported depletion of 1,4-dimethyl-dibenzothiophene (DMDBT), a persistent fuel oil contaminant.

It was shown that sensitizers can activate oxygen to form endo- and hydroperoxides of carbohydrates, which leads to derogation of natural fabrics and items of wood. It must be emphasized that many molecules which efficiently absorb light, behave like biradicals in excited state and are quenched with molecular oxygen producing oxygenated secondary radicals. These radicals, in turn, react quickly with any available surrounding molecule, and can change the surface of materials exposed to the light.

Combination of air pollutants, oxygen and light gives rise to, so called 'photochemical smog', which is recognized as a big problem in inhabited and industrialized areas with heavy traffics. Complex secondary reactions induced by sunlight are the major source of ozone in lower atmosphere, and it raises serious concerns about its influence to health.

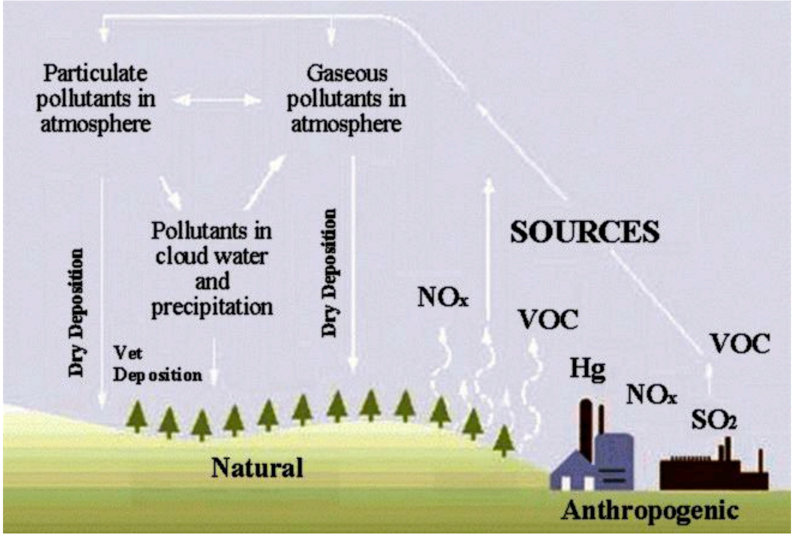


Figure 2. Circulation of pollutants in the air

Not only anthropogenic pollution is a source of reactive species in air. The numerous natural sources emit volatile (mostly organic) compounds to atmosphere. All living beings produce a variety of volatile organic compounds (VOC) which are constantly present in the troposphere.

The emission of organic compounds from plants contains in a high extent the various photoactive compounds, aromatics, aldehydes, ketones, etc…(almost all fragrances from plants). The photochemodynamics of these compounds has been studied recently.

5- In contact of oxygen and another material, upon the absorption of light quanta, a charge transfer(CT) process can occur, giving yield to pairs of ion-radicals.

Although this is the least studied mechanism of photooxidation, it is completely acceptable in theory. It can account for numerous instances of nonsensitized photooxygenations.

$$A + O_2 \xrightarrow{h\nu} \left[A^{\cdot +} + O_2^{\cdot -} \right] \longrightarrow products$$

The reliability of the CT mechanism can be justified by the following considerations.

The formation of radical-ion pairs is well known in the photochemistry of singlet exciplexes. The wave function for the excited state is described as:

$$\Psi = c1(A^*D) + c2(AD^*) + c3(A^{\cdot +}D^{-\cdot})$$

Triplet exciplexes can be treated in the same way, but cl and c2 are always much smaller than c3. In the ground state of the substrate-oxygen complex, the only attraction is due to the London forces. Namely, in the triplet state the exchange interactions are repulsive. The result is that in the ground state only a loose encounter complex can be formed between substrate and oxygen, having very short life time. Repulsion potential is practically the same in the excited triplet state as in the ground state. MNDO calculations show that the last energy transition in the X••••O2 complex is between HOMO, which is practically completely located on substrate moiety, and one of the SOMO orbitals on oxygen. In this way, the excitation is accompanied by the practically complete electron transfer from the substrate to oxygen. Excited states have a highly dipolar character and the two moieties, although not covalently bonded, are mutually attracted by a strong electrostatic force. The potential energy curve for the excited triplet state can be evaluated by superposition of the ground state repulsive potential and electrostatic attraction of two moieties. The depth of the PE minimum for the excited state is estimated as more than 100 kJ/mol. This can account for the considerably high stability of oxygen-substrate exciplex. It provides a relatively long lifetime, enabling different relaxation paths, such as the spin flip, hydrogen ion migration, etc. Oxygenations in the dark are also well known. The mechanism outlined above can also be valid for these oxygenations if it could be proved that nonpolar and CT PE curves cross not far from the equilibrium distance for nonpolar structure.

The actual reaction rate inherent to this mechanism is very low because it comprises a three body (substrate and oxygen molecules and photon) collision, which is a very rare event. It can become more plausible if the concentrations of pollutant molecules and/or oxygen is elevated. The surfaces of dispersed particles or of artifacts can serve as adsorbent on which the contact between various molecules is very probable. As the example, the partial pressure of oxygen in water can be 3.3 times higher that its partial pressure in the air. Moreover, the solvent can provide a kind of ‘cage’ which slower the dissociation of the encounter (instantaneous) complex between oxygen and other molecule.

Recently, several articles concerning direct photooxygenations were published. A truly non-sensitized photooxygenation was reported for the functionalization of carbon nanowires. The experiment was done using photoionization light, and resembles in a large extent to charge-transfer excitation. Another interesting example is a non-sensitized (direct) photooxygenation of luciferin analogs yielding hydroperoxides. A very convincing example of non-sensitized photo¬oxygenation was reported for pyrimido[5,4-g]pteridine-5-oxide, and end-product is usually a hydroxylated one.

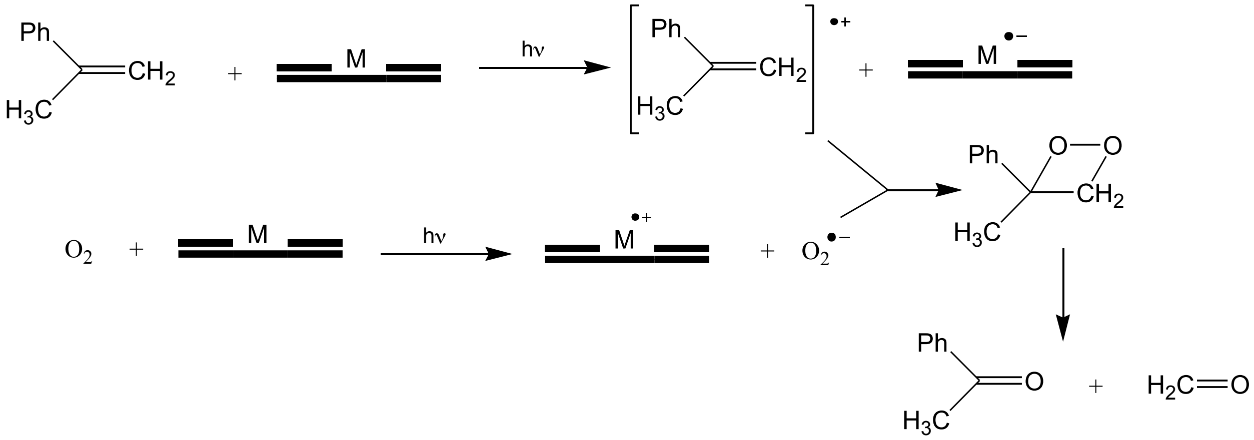
The photo-oxygenation of 8-methoxyberberinephenolbetaine was done without, and in the presence of a sensitizer (bengal rose), but with very different distribution of products.

In another study was proven that photooxygenation is not enhanced by the presence of Rose Bengal, an efficient sensitizer of singlet oxygen.

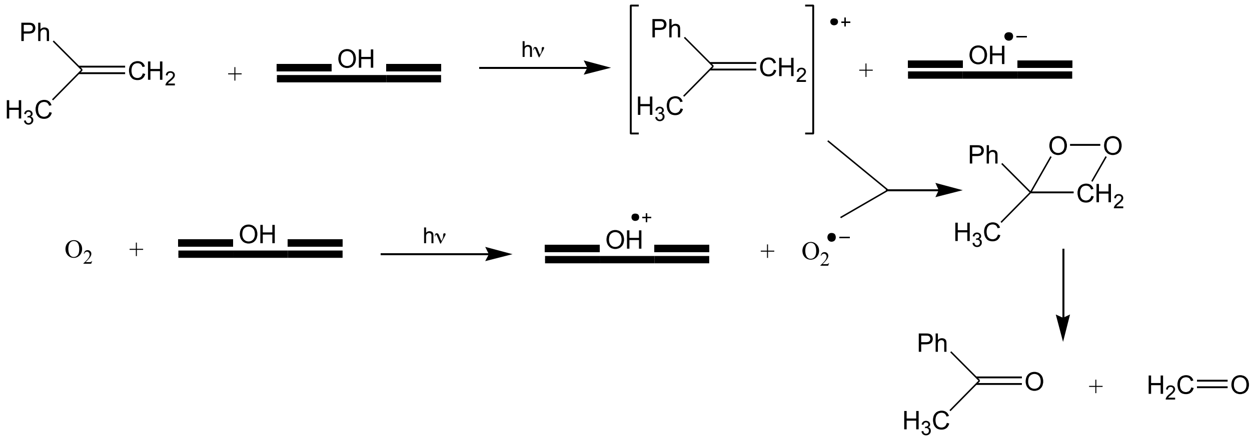
Obviously, a general mechanism for photo-oxygenation exists – one that doesn’t require sensitization. Just reactants and light are needed, in concentration just enough that reaction is not forbiddingly slow. All studied nonsensitized photo-oxygenations are reported in condensed phase.

A specific case of Lewis acid catalyzed photooxygenation was found when the photolysis of olefins adsorbed on silica or alumina was studied. Here, the surface of the adsorbent serves as the charge-transfer mediator for the catalysis of oxygenation. Two mechanisms are outlined:

For acidic solids:



For basic solids:



When 1,l-diphenylethylene, and its derivatives were used as substrate, Ph2CO and corresponding epoxides were obtained. A study on the photooxidation of organic impurities in water using thin film of titanium dioxide was reported as a possible efficient method for the purification of water. Almost the same mechanism was proposed for the photoactivated reaction of CO with O2 on a silica gel surface.

3. CONCLUSION

The light can markedly promote the processes of the ruination of artifacts. Particular role of light is in process of photooxygenation, which can happen through number of mechanistic paths. The photoactive molecules in their excited states can react with dioxygen in several modes: direct reaction as diradicals, or by the transfer of excitation to dioxygen giving rise to reactive singlet dioxygen.

Another, the most general mode of photooxygenation is the CT absorption of light quanta by molecules adsorbed on the solid surface, or dissolved in an adsorbed liquid film, and in contact with oxygen.

The reaction with dioxygen, can involve all kinds of substrates: organic, inorganic, natural, or artificial.

A general conclusion is self-evident. The protection of artifacts must involve the removal of pollution (both natural and anthropogenic) and (in the first place) protection against exposure to light.

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Stručni rad

FOTOHEMIJSKA AKTIVACIJA ZAGAĐIVAČA VAZDUHA I VEZA SA OČUVANJEM KULTURNOG NASLEĐA

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Izvod

Dobro je poznato da izloženost vazduhu i vremenskim prilikama dovodi do značajnog narušavanja stanja svih rukotvorina. U ovom radu ćemo anaizirati uticaj svetlosti (naročito sunčeve svetlosti) na značajno ubrzanje oksidacije i drugih promena kao posledica izloženosti atmosferskim prilikama. Može se identifikovati pet glavnih mehanizama efekta insolacije:1. Prvi je trivijalni- uticaj zagrevanja koji ubrzava sve hemijske procese 2. Fotoekscitacija materijala od koga je predmet izrađen, što ga čini reaktivnijim prema kiseoniku iz vazduha(i drugim prisutnim supstancama). 3. Senzibilizacija kiseonika putem ekcitacije u stanje singleta u kojem je on ekstremno reaktivan i može reagovati čak i sa inertnim materijalima.4. Fotohemijska transformacija isparljivih organskih jedinjenja(VOC), prvensveno aldehida i ketona, koja sa kiseonikom mogu dati organske kiseline i hidroperokside koji definitivno oštećuju većinu materijala. 5. U dodiru sa kiseonikom i nekim drugim materijalom, nakon apsorpcije kvantuma svetlosti može doći do procesa prenosa naelektrisanja, što dovodi do parova jon-radikala, koji se dalje mogu transformisati u razne reaktivne produkte.

***Ključne reči**: fotooksigenacija, hemijski mehanizmi, zagađivači vazduha.*