

Effect of light on humic substances: Production of reactive species

J.P. Aguer¹, C. Richard¹ and F. Andreux²

¹Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS, Université Blaise Pascal n° 6505, 63177 Aubière, France

²Centre des Sciences de la Terre, Université de Bourgogne, 6 boulevard Gabriel, 21000 Dijon, France

Under photochemical excitation, humic substances produce reactive species which can degrade a great variety of organic compounds. Solvated electrons, hydroxyl radicals, singlet oxygen and reactive triplet states were characterized using probe molecules and scavenging techniques. The quantum yield of formation of these species depends on the irradiation wavelength, on oxygen concentration and on the origin of the humic substances. Through their photoinductive properties, humic substances can be used to degrade pollutants.

Introduction

Humic substances (HS) absorb photons in the UV and the visible region of the solar spectrum up to 500 nm. The energy absorbed in this way lies within the range 58 – 98 kJ mol⁻¹ making a number of photochemical processes possible. In particular, reactive species capable of transforming a great variety of organic compounds can be produced. The continuing interest in the photochemical behavior of humic substances is due to their ability to act as depolluting agents by photoinducing the degradation of pollutants.

Here, we report the identification of some reactive species generated by the photochemical excitation of humic substances, the characterization being mainly based on the scavenging and probe molecule techniques. We also present the influence of irradiation wavelength, pH value and concentration of oxygen on the photoinductive properties of humic substances. Examples of photoinduced degradation of pollutants are given.

Experimental section

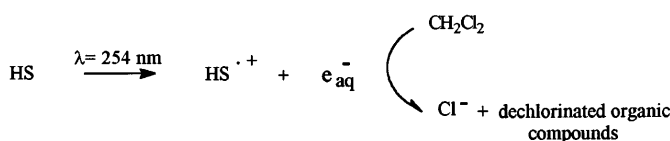
Humic and fulvic acids were purchased either from International Humic Substances Society (IHSS) or were extracted from different soils using a standard procedure [1]. Soils were sampled at three locations: A_h horizon from a

Mountain Ranker soil under grassland, B_h horizon from a Mountain Podzol under pine and heather, and A_p horizon from a cultivated brown leached soil. Experiments were also performed with Aldrich humic acids and humic acids synthesized from phenol [2]. Substrates were of the highest grade commercially available. Samples were prepared by solubilizing humic substances (10 to 100 mg L⁻¹) in distilled water buffered at pH = 6.5 with phosphates. Solutions were filtered on 0.45 μm Millipore filters then irradiated at 253.7 and 365 nm using germicidal and “black-light” lamps respectively. Irradiation was also conducted using polychromatic lamps (300 – 450 nm). Solutions were then analysed by High Performance Liquid Chromatography using a Waters chromatograph equipped with a photodiode array detector and a reverse-phase column (Merck Lichrospher; 250 mm × 3.9 mm; column packing, C₁₈, 5 μm). Mixtures methanol-water in proportion depending of the substrate tested were used as eluents at a flow of 1 mL/min. The chloride ions released in the phototransformations of dichloromethane and 3-(4'-chloro-phenyl)-1,1-dimethylurea (monuron) were titrated with a chloride specific electrode Orion.

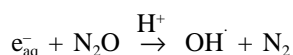
Results and discussion

Solvated electrons

The formation of solvated electrons was observed by laser-flash photolysis of humic and fulvic acids solutions [3]. These species are likely to result from the photoionization of phenolic moieties of humic substances because such a reaction is known to occur with phenols and phenolate anions [4]. At first, solutions of humic substances were irradiated at short wavelength (253.7 nm) using dichloromethane (2 × 10⁻² M) as substrate. The release of chloride ions was observed during irradiation. This finding shows that humic substances are able to photoinduce reductions. The quantum yield Φ of chloride formation which is defined as the ratio between the number of molecules formed over the number of photons absorbed during the same time was evaluated as 4.7 × 10⁻³.



Upon irradiation of neutral oxygen-free solutions of humic substances and 4-nitrophenol, no consumption of 4-nitrophenol was observed because the electrons did not react with 4-nitrophenol. The transformation of 4-nitrophenol into 4-nitropyrrocatechol was observed in solutions saturated with N_2O . This result is explained by the formation of the very oxidant hydroxyl radicals according to the reaction:

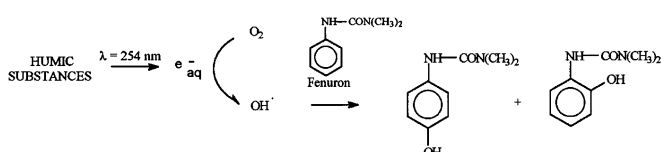


The degradation of 4-nitrophenol in N_2O -saturated solutions was 4 times more efficient at pH = 9.3 than at pH = 6. This is in a very good agreement with the hypothesis that photoejection occurs from the phenolic moiety. Various humic substances were found to photogenerate the solvated electrons at 253.7 nm and at longer wavelength (300 – 450 nm).

Hydroxyl radicals

The irradiation of air-saturated solutions of Aldrich humic acids and 4-nitrophenol at 253.7 nm yielded 4-nitropyrrocatechol as the main photoproduct, this formation being completely inhibited by the hydroxyl radical scavenger 2-propanol (0.5%). It means that solvated electrons are converted into hydroxyl radicals in the presence of oxygen. More specifically, the formation of hydroxyl radicals can be explained by the intermediate formation of hydrogen peroxide through the dismutation of O_2^-/HO_2^- followed by the photolysis of hydrogen peroxide.

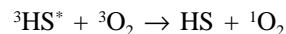
Aldrich humic acids photoinduced the transformation of 3-phenyl-1,1-dimethylurea (fenuron) at 253.7 nm. This phenyl-urea derivative was converted into ortho- and para-hydroxylated compounds in accordance with the involvement of hydroxyl radicals in the reaction.



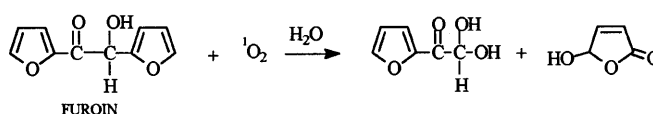
At 365 nm, 2-propanol (1%) did not inhibit the photoinduced transformation of fenuron in neutral medium indicating that hydroxyl radicals were not generated with such conditions. The photolytic process is impeded because hydrogen peroxide does not absorb photons at this wavelength. By contrast, an inhibiting effect of 2-propanol was observed again in acidic medium (pH 3.6). In this latter case, the reduction of hydrogen peroxide into hydroxyl radicals might involve ferrous cations photogenerated by excitation of Fe^{3+} -ligand. The reduction of hydrogen peroxide by $Fe(II)$ (Fenton-reaction) is expected to be much more efficient in acidic than in neutral solution because, in neutral medium, ferrous cations react quickly with oxygen.

Singlet oxygen

This excited state of oxygen is produced by energy transfer between triplet excited states of humic substances and oxygen in the ground state [5].



The singlet oxygen produced by photochemical excitation of our humic and fulvic acids was titrated using furoin as a probe molecule. This furan derivative was used because it yields a specific product, 1-furanyl-2-dihydroxyethanone, during singlet oxygen oxidation in water [6].



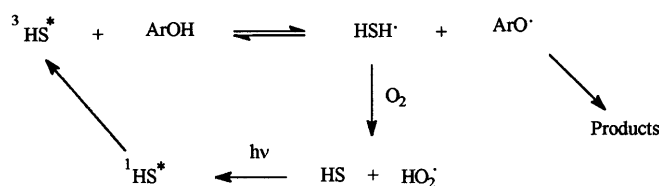
Humic substances were irradiated at 365 and 434 nm. Here, we evaluated the quantum yields of singlet oxygen formation by monitoring the formation of 1-furanyl-2-dihydroxyethanone. The involvement of singlet oxygen in the transformation of furoin was confirmed by the addition of a singlet oxygen quencher. Indeed, the formation of 1-furanyl-2-dihydroxyethanone was not observed in the presence of sodium azide (2.0×10^{-3} M). Significant differences in the ability of humic substances to photosensitize the formation of singlet oxygen were found, the quantum yields measured at 365 nm laying within the range 3.9×10^{-4} – 5.5×10^{-3} . The fulvic and humic acids extracted from the acidic Ranker soil were found to be the most efficient sensitizers.

For the Aldrich humic acids, the quantum yield of singlet oxygen formation decreased from 2.0×10^{-3} to 1.1×10^{-3} as the irradiation wavelength increased from 365 to 434 nm.

Reactive triplet states

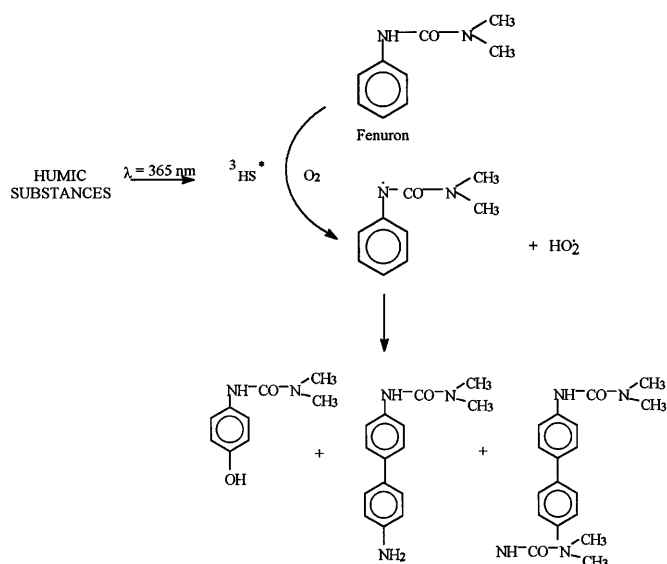
2,4,6-trimethylphenol was used as a substrate to study the photoinductive properties of humic substances. At 365 nm 2,4,6-trimethylphenol alone does not absorb light. Therefore it cannot be transformed by direct photolysis. However, this phenol was photodegraded by addition of all humic substances, except the synthetic humic acids. The rate of 2,4,6-trimethylphenol loss was greatly affected by oxygen. Indeed, the reaction was about 30 times faster in air-saturated than in deoxygenated solutions. In neutral medium, the disappearance of the substrate was neither affected by addition of azide anion nor by addition of 2-propanol. This result indicates that both hydroxyl radicals and singlet oxygen are not involved. Therefore a catalytic reaction is likely to occur. It has been previously proposed that peroxy radicals were responsible for the humic substances-mediated phototransformation of phenols [7]. Actually, the oxygen effect

Humic substances



observed is in a good agreement with an oxidation of the substrate by reactive triplet states as follows [8]:

Humic substances also photoinduced the transformation of fenuron at 365 nm. Again, the rate of consumption was faster in the presence of oxygen and the reaction was neither affected by the addition of 2-propanol nor by addition of azide anions showing that fenuron is oxidized by triplet states. The photoproducts were different from those obtained at 253.7 nm. The oxidation by triplets states at 365 nm gave the para-hydroxylated derivative and substituted biphenyles. The reactive triplet states of humic substances are likely to abstract the hydrogen atom from NH.



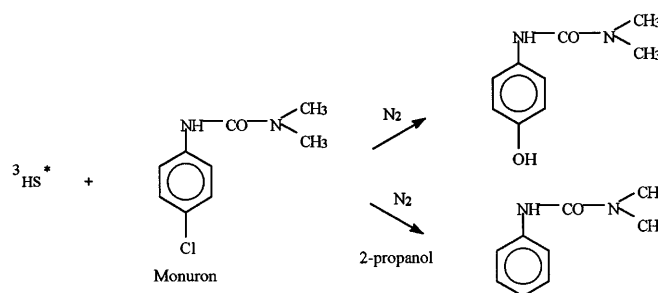
The ability of various HS to photosensitize the transformation of fenuron was compared. The first order rate constants of fenuron decrease laid within the range $1.8 \times 10^{-6} - 1.3 \times 10^{-4} \text{ s}^{-1}$ showing that the photoinductive properties of humic substances greatly depended on their origin (Tab. I). Moreover, fulvic acids were found to be better photosensitizers than humic acids.

The transformation of 3-(4'-chloro-phenyl)-1,1-dimethylurea (monuron) was also photoinduced by humic substances at 365 nm. Analytical and kinetic results indicated that an energy transfer mechanism was operating for the Ranker fulvic acids. As a proof, it was observed that the rate of monuron consumption was twice lower in the presence than in the absence of oxygen. Moreover, the photoproducts were the same as those obtained upon direct photolysis.

Table I. First order rate constants of fenuron consumption in the presence of various humic substances.

HS	$k \text{ (s}^{-1}\text{)}$
Soil fulvic acid (IHSS Standard)	1.3×10^{-4}
Ranker fulvic acid	9.0×10^{-5}
Brown leached soil fulvic acid	4.2×10^{-5}
Ranker humic acid	3.3×10^{-5}
Soil humic acid (IHSS Standard)	1.3×10^{-5}
Peat humic acid (IHSS Standard)	9.9×10^{-6}
Brown leached soil humic acid	9.4×10^{-6}
Podzol Bh humic acid	1.8×10^{-6}

Reaction of fenuron and monuron with triplet states of humic substances was also observed upon irradiation within the wavelength range 300 – 450 nm, however, a significant part of the transformations was attributed to hydroxyl radicals.



Conclusion

Through a systematic work, we have acquired a better insight into the complex photoreactivity of humic substances. Several reactive species such as electrons, hydroxyl radicals and singlet oxygen are produced by photochemical excitation of humic substances. Electrons that are generated by photoionization are converted into the highly oxidant hydroxyl radicals in the presence of oxygen. The formation of hydroxyl radicals is observed at $\lambda < 350 \text{ nm}$ whatever the pH, and at longer wavelength in acidic medium. Humic substances photosensitize the production of singlet oxygen on a large wavelength range. Reactive triplet states of humic substances are able to oxidize substrates bearing a labile hydrogen atom. In addition, in the case of the Ranker fulvic acids, energy transfer processes were shown to occur.

To get a better approach of the natural conditions, humic substances were irradiated within the range 300 – 450 nm. In these conditions, the solvated electrons, hydroxyl radicals

and reactive triplet states are produced. It can be concluded that humic substances are able to transform a great variety of organic substrates through the influence of solar-light. The ecological impact of the absorption of light by humic substances is difficult to evaluate however it should participate significantly to the auto-purification of superficial waters [9–11].

References

1. Barriuso, E.; Portal, J. M.; Andreux, F. *Org. Geochem.* **1984**, *4*, 115-118.
2. Aguer, J. P.; Richard, C. *J. Photochem. Photobiol. A* **1994**, *84*, 69-73.
3. Zepp, R. G.; Braun, A. M.; Hoigné, J.; Leenheer, J. A. *Environ. Sci. Technol.* **1987**, *21*, 485-490.
4. Creed, D. *Photochem. Photobiol.* **1984**, *39*, 563-575.
5. Zepp, R. G.; Wolfe, N. L.; Baughman, G. L.; Hollis, R. C. *Nature* **1977**, *267*, 421-423.
6. Aguer, J. P.; Richard, C. *Toxicol. Environ. Chem.* **1993**, *39*, 217-227.
7. Hoigné, J.; Faust, B. C.; Haag, W. R.; Scully, F. E.; Zepp, R. G. *Adv. Chem. Ser.* **1989**, *219*, 363-381.
8. Canonica, S.; Jans, U.; Stemmler, K.; Hoigné, J. *Environ. Sci. Technol.* **1995**, *29*, 1822-1831.
9. Sukul, P.; Moza, P. N.; Hustert, K.; Kettrup, A. *J. Agri. Food. Chem.* **1992**, *40*, 2488-2492.
10. Ahel, M.; Scully, F. E.; Hoigné, J.; Giger, W. *Chemosphere* **1994**, *28*, 1361-1368.
11. Jensen-Korte, U.; Anderson, C.; Spiteller, M. *Sci. Total Env.* **1987**, *62*