Photochemical behaviour of PAH in a liquid aerosol.

Bernard David[1], Christophe DUQUENOY, Joel SUPTIL, Jean-Luc BESOMBES

[1]University Of Savoie

PAHs are well known natural and anthropic contaminants emitted and dispersed in the environment. In the atmosphere, PAHs can be partitioned into the gas phase and the particulate phase. This last phase corresponds to liquid and solid aerosols. The overall PAHs reactivity will depend on their partition into these different compartments, according to their physicochemical properties. Under the atmospheric conditions including light, the oxidation of the organic matter occurs. This phenomenon is very important and has to be improved because it condition the atmospheric lifetime of the organic compounds and because it can lead to the formation of secondary aerosol which are expected to be imply in some human pathologies [1].

In this work, we focused our attention on the photochemical degradation of PAH present in an aqueous liquid aerosol. Pyrene has been used as PAH model molecule because it can be analysed at very low concentration (50 $ng.L^{-1}$) and because its reactivity in the aqueous phase is well known [2-3].

Most of the studies on the photochemistry of liquid aerosol are performed either in solution by assuming that the behaviour in a cloud is about the same that in an aqueous solution, or, in big chamber especially designed for the generation of aerosols. We present in this work a simple and practical reactor designed for the photochemistry of liquid and/or solid aerosol. With this reactor, it is possible to work in conditions close to those existing in the atmosphere. A 1.6 MHz piezoelectric ceramic allows to nebulize a saturated solution of pyrene in water (0.135 mg L^{-1}) in the 500 mL reactor. The cloud is then irradiated at 254 nm.

The characterization of the reactor will be presented especially by describing the aerosol volume formed and irradiated. The amount of liquid and gas volume in the generated aerosol itself are estimated. The partition of pyrene between the liquid and the gas phase in the aerosol has also been estimated by means of a SPME/GC/MS method.

The different phenomena occurring in the reactor were checked in order to get a photochemical rate constant of the pyrene degradation. The disparition of pyrene in the cloud result from the photolysis of pyrene in the aerosol, from its adsorption on the walls and also from a very low ultrasonic degradation. The pyrene degradation rate in the aerosol phase can be extracted from these different processes. A comparison is then done between the degradation rate of pyrene in the aqueous solution and in the aerosol assuming an homogeneous actinometry in the reactor.

In order to understand the photochemical mechanism of pyrene degradation in the aerosol phase, experiments have been carried out in water/methanol mixtures for different compositions. According to the polarity of the media, the degradation rates are higher in presence of pure water than pure methanol, and intermediate for the different compositions. The formation of a primary ionic species is then suspected and could be the pyrene radical cation which has been already detected in solution [3].

Finally, some perspectives are given on the different possibilities of evolution of this reactor.

[1] R. Peled, M. Friger, A. Bolotin, H. Bibi, L. Epstein, D. Pilpel and S. Scharf, Fine particles and meteorological conditions are associated with lung function in children with asthma living near two power plant, Public Health, 119, 5, 418-425, 2005.

[2] A.Boscher, B.David, S.Guittonneau, Photodegradation of pyrene on solid phase, in Environnemental Chemistry, Green chemistry and pollutants in ecosystems, E.Lichtfouse, J.Schwartzbauer, R.Didier (Eds.) Springer Verlag, 2005.

[3] A.Boscher, PhD, Photodégradation du pyrène en solution aqueuse et en phase adsorbée, Université de Savoie, Feb. 2005.