Formaldehyde production during sunscreen agent 2-ethylhexyl 4-(dimethylamino)benzoate demethylation

It is well known that formaldehyde is a toxic and carcinogenic pollutant causing severe problems on humans' health and aqueous ecosystems. Therefore, many attempts have been made to determine the sources of formaldehyde emission to the environment. Among anthropogenic paths, personal care products (PCPS) degradation and photodegradation processes under the influence of reactive oxygen and chlorine species (ROCS) deserve particular attention.

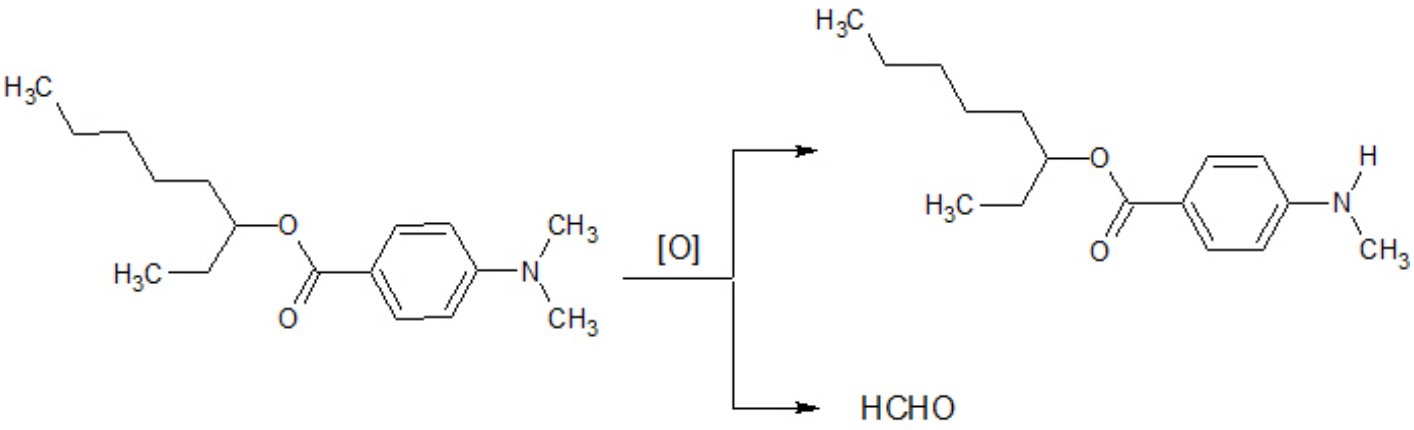

Fig. 1. ODPABA demethylation.

Our research group is focused on the environmental fate of UV filters. The main goal of this project is to examine the effect of disinfectants and water treatment conditions on degradation of popular sunscreen agents such as octyl methoxycinnamate (OMC) and 2-ethylhexyl 4-(dimethylamino)benzoate (ODPABA). The reaction mixtures are usually analyzed using chromatographic methods and UV-VIS spectroscopy. In order to explain the nature of degradation paths, the results of our quantum-chemical calculations are analyzed including thermochemical and reactivity aspects. The latest results of our work showed that ODPABA undergoes demethylation in the presence of UV light and disinfectants, H_2O_2 and NaOCl yielding formaldehyde (Fig. 1).

As we found, in the case of ODPABA/UV, ODPABA/H2O2/UV and ODPABA/NaOCl/UV systems demethylation proceeded significantly faster than in case of non-irradiated samples (Fig. 2). This can be explained by analyzing the nature of demethylation reactions. There are two possible paths, namely radical mechanism proceeding via one-electron oxidation and ionic mechanism involving electrophilic attack on the amino group. The quantum-chemical calculations showed that ODPABA nitrogen atom is highly susceptible for the electrophilic attack of HOCl which probably occurs in case of non-irradiated reaction mixture. It is well known, that radical reactions are more favored when samples are subjected to the UV light irradiation.

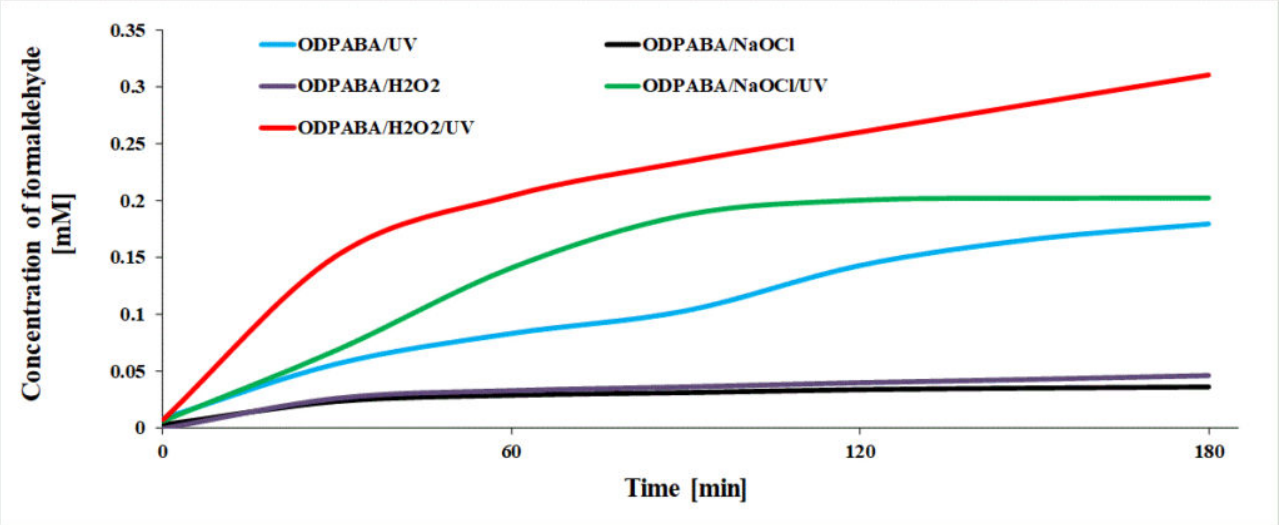

Fig. 2. The kinetic curves of formaldehyde formation via ODPABA demethylation under different conditions.

Therefore, in the case of ODPABA/UV, ODPABA/H2O2/UV and ODPABA/NaOCl/UV systems, demethylation proceeds probably according to the radical mechanism. This mechanism can be described by the thermodynamic analysis performed using molecular modeling tools. As we found, hydrogen atom abstraction from the methyl group attached to the amino nitrogen is thermodynamically more favorable than from 2-ethylhexyl group. This shows that $N(CH_3)_2$ group oxidation is probably the initial stage of ODPABA radical degradation process.

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Publication

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