

Effect of UV radiation on the fastness of selected UV filters

Alicja GACKOWSKA, Jerzy GACA - Chair of Chemistry and Environmental Protection, Faculty of Chemical Technology and Engineering, University of Technology and Life Sciences, Bydgoszcz

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Introduction

Escalation of radiation intensity reaching the Earth caused that the natural protection of living organisms against the radiation become insufficient. A high dose of radiation is also harmful to surfaces made of plastics, paint coatings, textiles, rubbers and pigments contributing to their degradation. In order to protect human skin from the harmful effects of UV radiation, the compounds which absorb UVA within the range from 320 to 400 nm and UVB from 290 to 320 nm are introduced into everyday products such as hand creams, cosmetics, hairsprays, body lotions, hair dyes, shampoos, etc [1]. These compounds are commonly named UV filters. Both organic and inorganic substances, which fulfil the role of UV filters are known [2]. Organic UV filters usually consist of one or more aromatic rings which are sometimes joined by double carbon-carbon bond or carbonyl group. Benzophenone derivatives or β -diketones, and particularly 1,3-diarypropane-1,3-dione derivatives are UV filters among others [3, 4].

Environmental studies showed presence of UV filters in surface waters from recreational areas [5-7], swimming pools [1, 8, 9] and in municipal wastewater [10, 11]. Although the use of UV filters is limited compared to other chemicals (such as soaps and detergents), their impact on the environment may be important, since most UV filters are highly lipophilic and penetrating directly into surface waters, they can be accumulated by living organisms. The more that UV filters present in swimming areas can be converted into other compounds with the results that there is a possibility of contact with human body, both the filters and products of their conversion which can be far more harmful than original compounds. In addition, degradation of UV filters may be intensified by the presence of environmental factors (e.g. oxidants or salinity) in consequence of which new pollution in water environment can be generated. Properties of UV filters show that different mechanisms can be responsible for their behavior in the environment. So far no answer was found to the question whether the negative effects produce the UV filters or their metabolites. The authors of some studies suggest that by-products resulting from decomposition of filters can have an adverse impact on human health by their direct contact with the skin surface [3, 5].

The aim of this study was to examine the photostability of selected UV filters in the presence of an oxidizing agent and sodium chloride. Hydrogen peroxide which is commonly used in wastewater and water treatment was selected as an oxidizing agent.

Moreover, due to the presence of chloride ions in both surface waters and in wastewater, and taking into account the literature reports stating that chlorides play an important role in the photochemical process of UV filters removal from surface waters [5, 8, 12], studies on the effect of sodium chloride on the fastness of UV filters were carried out.

Experimental

The following UV filters were used in our studies: 1-(4'-t-butylphenyl)-3-(4''-methoxyphenyl)propane-1,3-dione (MBBM), 1,3-bis-(4'-methoxyphenyl)propane-1,3-dione (MMBM), 1-(4'-t-methoxyphenyl)-3-phenylpropane-1,3-dione (MBM) and crown ether $C_{12}H_{24}O_6$ (CE). The following systems were studied: MMBM/UV; MMBM/UV/ H_2O_2 ; MMBM/UV/ H_2O_2 /NaCl; MBBM/UV; MBBM/UV/ H_2O_2 ; MBBM/UV/ H_2O_2 /NaCl; MBM/UV; MBM/UV/ H_2O_2 ; MBM/UV/ H_2O_2 /NaCl MBBM/ H_2O_2 /NaCl/CE. Concentrations of reagents were as follows: UV filters

10^{-5} mol/l; H_2O_2 0.25 mol/l; NaCl 0.025 mol/l. Effect of UV radiation on the fastness of UV filters was studied using xenon lamp of KZ6103 type. Changes in absorption maximum of the compound were monitored by Agilent 8452 A spectrophotometer.

UV filters used in the studies were obtained from the Department of Chemical Organic Technology and Petrochemistry, Faculty of Chemistry, Silesian University of Technology.

Results and discussion

Studies on fastness of MMBM, MBBM and MBM in methanol showed that these compounds were resistant to UV radiation. Introduction of oxidizer (hydrogen peroxide) into the system resulted in changes in the fastness of the compounds studied. The most stable compound was MBM. Absorbance at $\lambda_{max} = 354$ nm was not changed after 180 minutes of radiation. In case of MMBM, absorbance at $\lambda_{max} = 362$ nm was reduced by 10%. It was found that prolongation of the exposure time to 300 min resulted in decrease by further 30%. However, in the system with participation of MBBM, absorbance at $\lambda_{max} = 360$ nm decreased by 20% (Fig. 1).

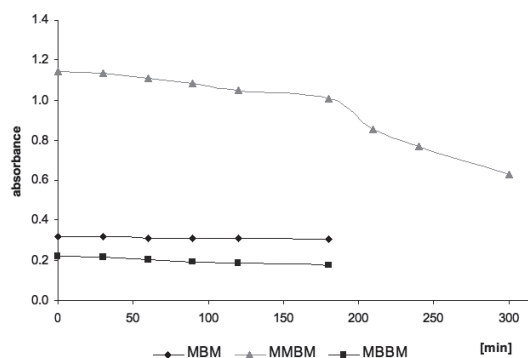


Fig. 1. Effect of UV radiation on the system Filter/ H_2O_2

The results obtained indicate that the selected UV filters are resistant to UV radiation. However, in the presence of an oxidizing agent their stability decreases. It is known that hydrogen peroxide under UV radiation is a source of radicals, which in turn can attack the filter particles forming new radicals, derivatives of diketones.

Due to the possibility of the potential contact of UV filters with salty waters, studies on the system UV/hydrogen peroxide in the presence of sodium chloride were conducted. In reaction with MBBM, after

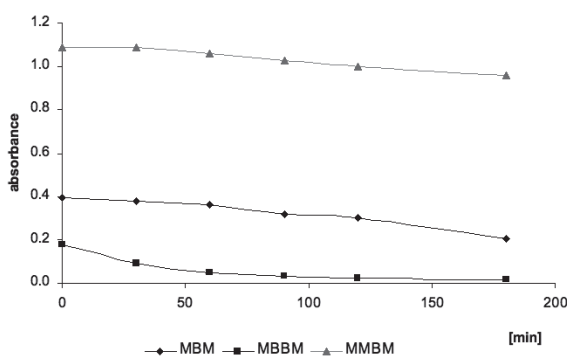


Fig. 2. Effect of UV radiation on the system: Filter/ H_2O_2 /NaCl

180 minutes, adsorption was reduced by 90% and in the system with MBM by 50%. In the case of reaction with MMBM, no impact of sodium chloride was observed (Fig. 2).

Interesting is the effect of sodium chloride. Decrease in the absorbance at λ_{\max} was observed in two of the three systems investigated with NaCl. It can be assumed that chloride ions can participate in reaction with hydrogen peroxide to form derivatives of HOCl, which in turn in reaction with hydrogen peroxide contributes to formation of chlorine radicals. These radical, similarly as OH \cdot , attack UV filters resulting in their photodegradation. Taking into account previous studies on the system H $_2$ O $_2$ /NaCl/UV with other compounds [13], it was hypothesized that not only Cl $^-$ ions contribute to the degradation of the UV filters but also Na $^+$ ions present in the system. In order to test the hypothesis assumed, crown ether that binds Na $^+$ ions was introduced into the system containing MBBM, hydrogen peroxide and sodium chloride. It was found that after 180 minutes of radiation of MBBM/H $_2$ O $_2$ /NaCl/CE system, absorption value decreased by 50%, while it decreased by 90% without participation of crown ether (Fig.3). The results obtained confirm the effect of Na $^+$ ions on the degradation of MBBM.

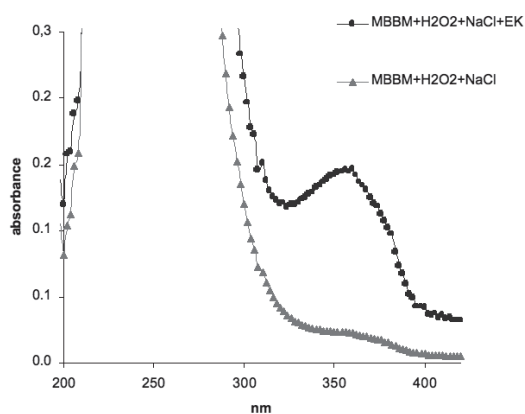


Fig. 3. Effect of crown ether (CE) on photostability of MBBM/H $_2$ O $_2$ /NaCl system

Studies on the fastness of filters revealed that all three compounds are photostable in polar solvent. In order to verify whether change in solvent to non-polar one will affect the fastness of filters, reaction with MBBM in carbon tetrachloride was performed. It was observed that the enol form of this compound decomposes relatively quickly with transition to ketone form, what was proved by the decreasing value of the absorbance at $\lambda = 360$ nm, and increasing at $\lambda = 288$ nm (Fig. 4).

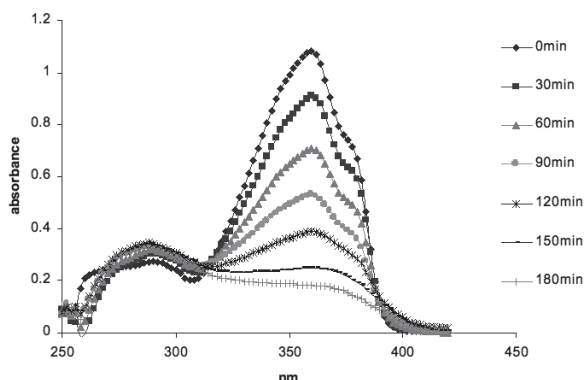


Fig. 4. Effect of UV radiation on photodegradation of MBBM in CCl $_4$

Conclusions

Studies on model systems showed that the compounds studied were resistant to UV radiation in polar solvent. Moreover, they are also resistant to the action of sole oxidizing agent or sodium chloride. However, in H $_2$ O $_2$ -UV system photodegradation of filters occurs. On the example with participation of MBBM, it was observed that photodegradation of filter was intensified when NaCl was additionally introduced into H $_2$ O $_2$ -UV system NaCl. At this stage of studies, the

authors can not answer the question why the presence of sodium chloride plays such an important role in this process. While the effect of chloride ions can be explained by changes occurring at the stage chloride ion-hydrogen peroxide, it is difficult to find answer what is the role of Na $^+$ ion. Different course of reaction was observed when the irradiation process was conducted in a non-polar solvent i.e. carbon tetrachloride.

Literature

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Alicja GACKOWSKA Ph.D.(Eng), is a graduate of Faculty of Technology and Chemical Engineering, University of Technology and Agriculture (now: University of Technology and Life Sciences) (1999). She got her doctoral degree at Faculty of Technology and Chemical Engineering UTA in Bydgoszcz (2006). She is co-author of 11 papers published in scientific journals and 15 posters at national and international conferences.

Jerzy GACA Ph.D.(Eng) Professor, is a graduate of Faculty of Chemistry (A. Mickiewicz University, 1963). He got his doctoral degree at Faculty of Chemistry (M.Kopernik University, 1976), qualification as assistant professor at Faculty of Chemistry (University in Lipsk, 1990). He gained the title of professor in 2007. In 2002, he was awarded honorary doctorate of Technological University in Jarosław (Russia). He has many awards and prizes including the Prize of Minister of Higher Education and the Marshal of Voivodeship. He is the author and co-author of: 22 chapters in books and monographs, 191 papers in scientific and technical journals, 32 patents, 83 papers for industry, 27 implementations and 210 presentations at national and international conferences. At present, he is employed as professor at University of Technology and Life Sciences.