Factors affecting the rate of benzo[*a*]pyrene decomposition in non-polar system – a model study

BOŽENA SKLÁRŠOVÁ – ALENA BEDNÁRIKOVÁ – EMIL KOLEK – PETER ŠIMKO

SUMMARY

Decomposition of benzo[*a*]pyrene (BaP) was studied at two different light wavelengths, i.e. 254 nm and 365 nm in a non-polar medium (*n*-hexane) at concentrations 50, 100 and 150 $\mu g \cdot l^{-1}$. At chosen time intervals, BaP concentration was measured by HPLC using fluorescence detection. Comparing rate constants k and half-lives $\tau_{1/2}$ it was found that decomposition at 365 nm was 15.3 times faster in comparison with the decomposition at 254 nm. The decompositions obey the first order kinetics. Considerable effect had addition of food antioxidants, 2,6-di-*tert*-butyl-4-methylphenol (BHT) and *o*-methoxyphenol (guaiacol), which both accelerated the rate of BaP decomposition – BHT by 1.17 times and guaiacol even 1.45 times. This means that both antioxidants had pro-oxidant effects on BaP. These findings may represent a basis for a new approach to decrease PAH content in foods, where their presence is due to the applied production technology.

Keywords

benzo[*a*]pyrene; photolysis; decomposition; kinetics; BHT; guaiacol; prooxidant effects

Polycyclic aromatic hydrocarbons (PAH) include the largest class of known environmental carcinogenic compounds. Some of them, even though not carcinogenic, may act as synergists [1]. PAH are extensively found in various foods as a result of technological procedures such as grilling, drying, frying and mainly smoking [2–3]. An environmentally relevant aspect of PAH toxicity is that it can be increased by solar radiation [4–8]. As known, PAH contain two or more conjugated benzene rings that facilitate the absorption of ultraviolet A (UVA) radiation (320–400 nm), ultraviolet B (UVB) radiation (290–320 nm) and, in some instances, visible light (400–700 nm). This leads to photoactivation of PAH and increase their toxicity via the production of singlet oxygen and photomodification of original molecules, which results in the formation of so-called oxy-PAH products [5, 8–12]. Many of the photoproducts generated through environmental photomodification exhibit greater toxicity than the parent PAH, and have the potential to generate toxic compounds that could negatively impact living systems and human health. On the other hand, photodegradation is an important transformation pathway for most PAH, because this process preferentially attacks the same tertiary carbon atoms that tend to block biodegradation [13]. As already proven, PAH deposited on the surface of smoked food are partially oxidized due to the presence of light and oxygen [14–15]. However, the influence of light and antioxidants on PAH has not been studied so far. So, the aim of this work was to study the behaviour of benzo[*a*]pyrene (BaP) as a representative PAH in non-polar liquid media at different wavelengths and in the presence of food antioxidants such as butylhydroxytoluene and guaiacol.

MATERIALS AND METHODS

Chemicals

Benzo[*a*]pyrene (BaP) of analytical grade was purchased from Supelco (Bellefonte, Pennsylvania, USA) in a solid state. Solvent *n*-hexane of analytical grade was purchased from Merck (Darmstadt, Germany). The solvent was rectified

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just before use in a distillation apparatus. Antioxidants 2,6-di-*tert*-butyl-4-methylphenol (BHT) and *o*-methoxyphenol (guaiacol) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA).

Photolysis experiments

The photolysis experiments were carried out in a 75 ml glass reactor, immersed in a thermostatic bath (Photochemical Reactors, Reading, United Kingdom). The reactor was equipped with a central inlet at its top to place a quartz immersion for 6 watt low pressure UV lamp (λ = 254 nm) and xenone lamp (λ = 365 nm).

At first, degradation of BaP in *n*-hexane was studied at λ = 254 nm at initial concentrations of 50, 100 and 150 $\mu g \cdot l^{-1}$. The samples for analysis were taken at defined time intervals and analysed by HPLC. Then, the same experiments were carried out at λ = 365 nm. Finally, the influence of antioxidants on BaP decomposition was studied. Measurements were realized at a BaP concentration of 100 $\mu g \cdot l^{-1}$ in *n*-hexane at 365 nm and at two different concentrations of antioxidants, i.e. 100 $mg \cdot l^{-1}$ and 1 $g \cdot l^{-1}$ for BHT and guaiacol, respectively.

HPLC

HPLC analyses were carried out using the Shimadzu equipment (Kyoto, Japan) consisting of solvent delivery module LC-20AD, autosampler SIL-20A, degasser DGU-20A5, column oven CTO-20A, communication bus module CBM-20A, diode array detector SPD-M20A, and fluorescence detector RF-10AXL. The analytical separation was performed on Zorbax Eclipse XDB-C18 column (50 mm × 4.6 mm, 1.8 μm; Agilent Technologies, Palo Alto, California, USA) using isocratic elution with methanol at a flow rate of 0.5 $ml \cdot min^{-1}$ at 35 °C. Fluorescence detector operated at excitation wavelength of 300 nm and emission wavelength of 410 nm.

RESULTS AND DISCUSSION

Photolysis of BaP was studied in *n*-hexane as a non-polar medium since PAH, in general, are liphophilic compounds and tend to migrate and concentrate in liphophilic foods such as fats, oils or adipose tissues. As shown in Fig. 1 and Fig. 2, the dependences of concentrations on time were exponential which is typical for first-order reactions. Indeed, this presumption was proven on the basis of a calculation of the reaction order using the equations 1, 2 and 3.

$$-\frac{dc}{dt} = kc^n \tag{1}$$

$$c = \frac{c_0}{\sqrt[n-1]{1 + c_0^{n-1}(n-1)kt}} \quad \text{for } n \neq 1 \tag{2}$$

$$c = c_0 \cdot e^{-kt} \quad \text{for } n = 1 \tag{3}$$

where c_0 is initial concentration of BaP, c is the concentration in given time, t is duration of the experiment, n is reaction order and k is rate constant.

The computation itself was performed by programme Origin Pro 7.0 (OriginLab, Northampton, Massachusetts, USA). The results are listed in Tab. 1. The calculated data show that the oxida-

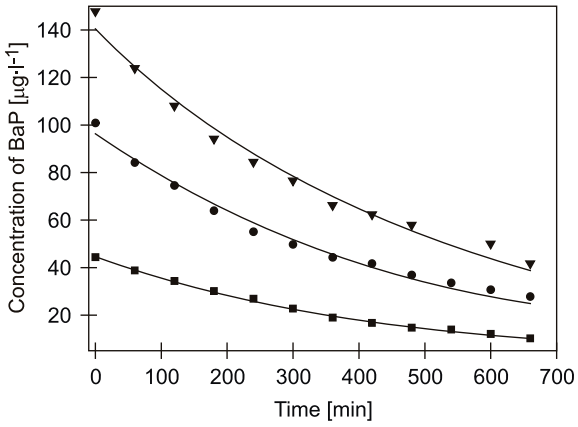

Fig. 1. Course of BaP decomposition in *n*-hexane at 254 nm at the initial concentration of 50, 100 and 150 $\mu g \cdot l^{-1}$.

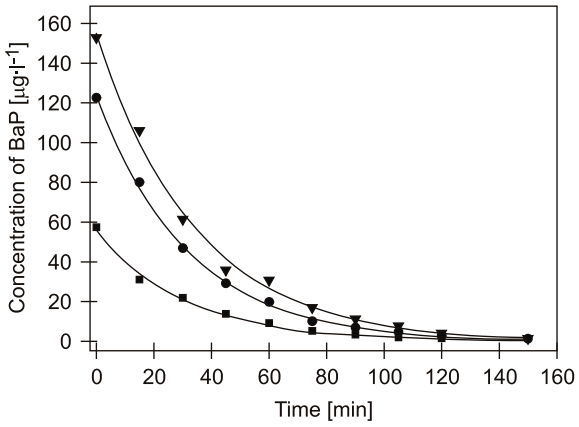

Fig. 2. Course of BaP decomposition in *n*-hexane at 365 nm for at the initial concentration of 50, 100 and 150 $\mu g \cdot l^{-1}$.

Tab. 1. The values of the reaction order of BaP decomposition in *n*-hexane at 254 nm and 365 nm.

Concentration of BaP [μg.l^{-1}]	Reaction order *n*	
	254 nm	365 nm
50	0.99	1.00
100	1.18	1.00
150	1.15	1.00

Tab. 2. The values of rate constants and half-lifes of BaP decomposition in *n*-hexane at a wavelength of 365 nm with and without the addition of antioxidants.

k [min^{-1}]	$\tau_{1/2}$ [min]	Conditions
0.00205	338.12	*n*-hexane, 254 nm
0.03143	22.05	*n*-hexane, 365 nm
0.04570	15.17	*n*-hexane + 100 mg·l^{-1} guaiacol, 365 nm
0.03699	18.74	*n*-hexane +100 mg·l^{-1} BHT, 365 nm

tion of BaP can be regarded as first-order reaction and confirm the exponential dependence of concentration on time. Very important factor affecting the rate of BaP decomposition is the irradiation wavelength. Comparing the calculated data of rate constants and half-lives, it was found that the decomposition of BaP at 365 nm proceeds 15.3 times more rapidly in comparison with the decomposition at 254 nm. The rate constants and half-lives are listed in Tab. 2. The effect of the addition of food antioxidants to BaP was very interesting. In general, these compounds protect food components against oxidation processes after addition to prolong original properties of foods. Surprisingly, both tested antioxidants i.e. BHT and guaiacol accelerated BaP oxidation, as shown in Figs. 3 and 4. As the rate constant and half-lives show, BHT accelerated decomposition of BaP by 1.17 times and of guaiacol even 1.45 times.

CONCLUSIONS

Rate of decomposition of BaP strongly depends on light wavelength, and it is 15.3 times faster at 365 nm in comparison to the decomposition at 254 nm. Food antioxidants have accelerating effect on the rate of BaP decomposition where BHT decimposed 1.17 times and guaiacol even 1.45 times faster. The study of components formed during BaP oxidation in the presence of antioxidants will be the subject of further research. These findings may represent a basis for a new approach to decrease PAH content in foods, where their presence is due to the applied production technology.

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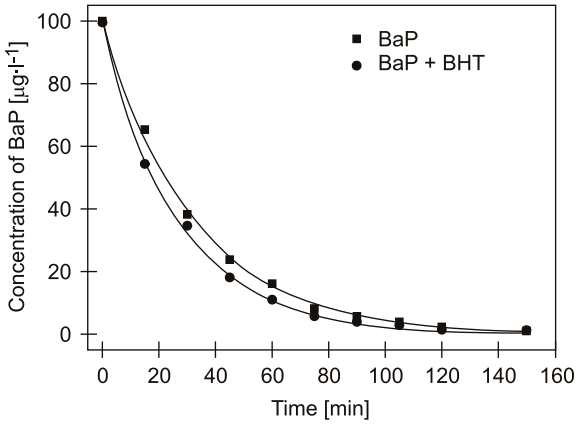

Fig. 3. BaP decomposition in *n*-hexane at 365 nm at the initial concentration of BaP of 100 μg·l^{-1} alone and in the presence of 100 mg·l^{-1} BHT.

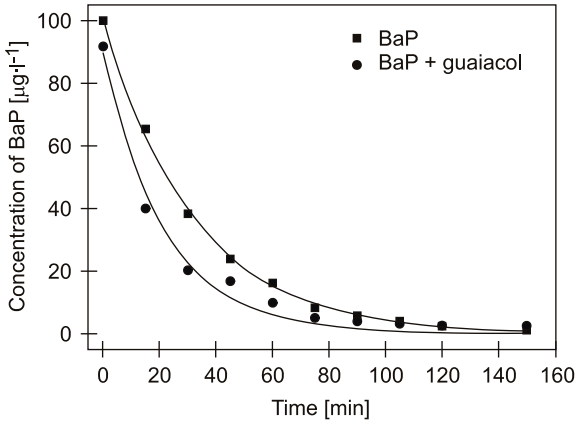

Fig. 4. BaP decomposition in *n*-hexane at 365 nm at the initial concentration of BaP of 100 μg·l^{-1} alone and in the presence of 100 mg·l^{-1} guaiacol.

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