

Experimental and theoretical studies on the photodegradation of 2-ethylhexyl 4-methoxycinnamate in the presence of reactive oxygen and chlorine species

Research Article

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Abstract: 2-Ethylhexyl 4-methoxycinnamate (EHMC) is one of the most commonly used sunscreen ingredient. In this study we investigated photodegradation of EHMC in the presence of such common oxidizing and chlorinating systems as H₂O₂, H₂O₂/HCl, H₂O₂/UV, and H₂O₂/HCl/UV. Reaction products were detected by gas chromatography with a mass spectrometric detector (GC-MS). As a result of experimental studies chloro-substituted 4-methoxycinnamic acid (4-MCA), 4-methoxybenzaldehyde (4-MBA) and 4-methoxyphenol (4-MP) were identified. Experimental studies were enriched with DFT and MP2 calculations. We found that reactions of 4-MCA, 4-MBA and 4-MP with Cl₂ and HOCl were in all cases thermodynamically favorable. However, reactivity indices provide a better explanation of the formation of particular chloroorganic compounds. Generally, those isomeric forms of mono- and dichlorinated compounds which exhibits the highest hardness were identified. Nucleophilicity of the chloroorganic compounds precursors were examined by means of the Fukui function.

Keywords: 2-ethylhexyl 4-methoxycinnamate • Chlorination • Oxidation • Photodegradation • Stability
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1. Introduction

Substances which absorb UV light and convert it into heat, fluorescence or phosphorescence, are often used as cosmetics ingredients and in photostabilization of polymeric materials and paints [1]. Because cinnamic acid derivatives convert absorbed light energy into heat with excellent efficiency [2,3] they are among the most popular UV sunscreen ingredients. Recently there has been a growing interest in the research of sunscreens [4-10].

There are many studies dealing with photodegradation of different compounds used as polymer additives

[11], personal care products [10,12], dyes [13], and pharmaceuticals [14,15]. From the usability point of view, the UV absorbers should exhibit high photostability. Nevertheless there are studies which show that these compounds are relatively light-sensitive in environments of different polarity such as water [4,12], methanol [16], and petroleum jelly [17]. MacManus-Spencer *et al.* [12] found that 2-ethylhexyl 4-methoxycinnamate (EHMC) undergoes photolysis which results in formation of 4-methoxybenzaldehyde and 2-ethylhexyl alcohol. From the theoretical point of view, stability of organic compounds can be evaluated using thermochemical calculations. In many cases however the thermodynamic

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Table 1. Molar proportions and concentrations of the reagents in the studied systems.

Molar proportion	Concentration [M]		
	EHMC	H ₂ O ₂	HCl
1:10:10	0.005	0.05	0.05
1:5:10	0.005	0.025	0.05
1:10:5	0.005	0.05	0.025

approach does not provide a complete description and hence reactivity indices should be taken into account. It is well known that reactive oxygen and chlorine species (ROCS) are formed in many natural and industrial processes. Hydrogen peroxide and its mixtures with HCl are the sources of many various chlorinating and oxidizing agents such as OH[•], HO₂[•], O₂, Cl[•], Cl⁻, Cl⁺, Cl₂, HOCl, H₂OCl⁺, ClO⁻ [18]. According to Nakajima *et al.* [19] chlorinated EHMC derivatives can be formed during EHMC photodegradation in the presence of HOCl. As we reported in our previous paper, chlorinating and oxidizing agents significantly enhance photodegradation of UV absorbers [20]. The main objective of this study has been to research EHMC photodegradation in the presence of common oxidizing and chlorinating model systems such as H₂O₂, H₂O₂/HCl, H₂O₂/UV and H₂O₂/HCl/UV [14,18,21-23]. In order to achieve this goal the experimental methods, such as GC/MS chromatography, spectrophotometric measurements as well as the theoretical tools (thermodynamic calculations, reactivity indices) were applied.

2. Experimental procedure

2.1. Materials and methods

All chemicals were used without further purification. Analytical standard of 2-ethylhexyl 4-methoxycinnamate (EHMC) (98%) was obtained from ACROS Organics (USA) and was kept in lightproof container at 4°C. Other chemicals used in the studies, methanol MeOH (96%), ethyl acetate, H₂O₂ (30%) and HCl (36%) were purchased from POCH S.A. (Poland).

2.2. Reaction conditions

First, methanolic solutions of EHMC, H₂O₂ and HCl were prepared. These solutions were then mixed in molar proportions according to Table 1. 900 mL of each mixture was subjected to the UV light using a photoreactor equipped with a medium pressure mercury lamp (Heraeus, TQ 150W), which emits radiation in the 200-600 nm range. The mixtures in the photoreactor

were stirred using a magnetic stirrer (200 rpm). The temperature of the system was kept at 20°C.

2.3. Analytical methods

Changes in EHMC concentration were monitored using Agilent 8452A spectrophotometer. The absorbance changes of the EHMC solution were measured at $\lambda_{\max} = 310$ nm. Samples of 0.1 ml were taken from the reactor at different time intervals and diluted 60 times with methanol before measuring the spectra. All spectrophotometric measurements were performed in standard quartz cuvettes of 1 cm optical path. Methanol was used as a blank sample. Each photodegradation experiment was performed three times and the mean values of absorbance were used for kinetic analysis.

Qualitative analyses of reaction mixtures were performed according to the following procedure. After UV radiation, solutions (ca. 900 mL) were concentrated to a volume of 1 mL using rotary vacuum evaporator ($p=122$ mbar, $t=40^\circ\text{C}$). In the next step, 0.1 mL of concentrate was diluted with 1 mL of ethyl acetate. So prepared samples were analyzed by HEWLETT PACKARD 5890 gas chromatographer equipped with a mass spectrometric detector and the ZB-5MS column (0.25 mm \times 30 m \times 0.25 μm). The operating conditions were as follows: 100°C-10°C min⁻¹-200°C/2 min-10°C min⁻¹-300°C 2 min⁻¹. The volume of the sample was 1 μL . Helium was used as a carrier gas. The schematic diagram of the experimental procedures is illustrated in Fig. 1.

3. Calculation details

All geometry optimizations and thermodynamic analysis, were performed applying the Becke three-parameter (B3) hybrid method [24-26] with the Lee-Yang-Parr (LYP) functional [27] and 6-31+G(d,p) basis set (B3LYP/6-31+G(d,p)). For open-shell systems, the spin-unrestricted calculations were applied (UB3LYP/6-31+G(d,p)). In order to get more accurate results, a large integration grid and tight convergence criteria were used. Vibrational analysis was performed for all compounds and no imaginary frequencies were found. Changes of thermodynamic functions, enthalpy (ΔH) and Gibbs free energy (ΔG), were calculated for standard conditions ($T=298.15$ K and $P=101325$ Pa). For each compound only the most stable conformation of a molecule was taken into account (global minima on the potential energy hypersurface). In order to include the solvent effect the self-consistent reaction field

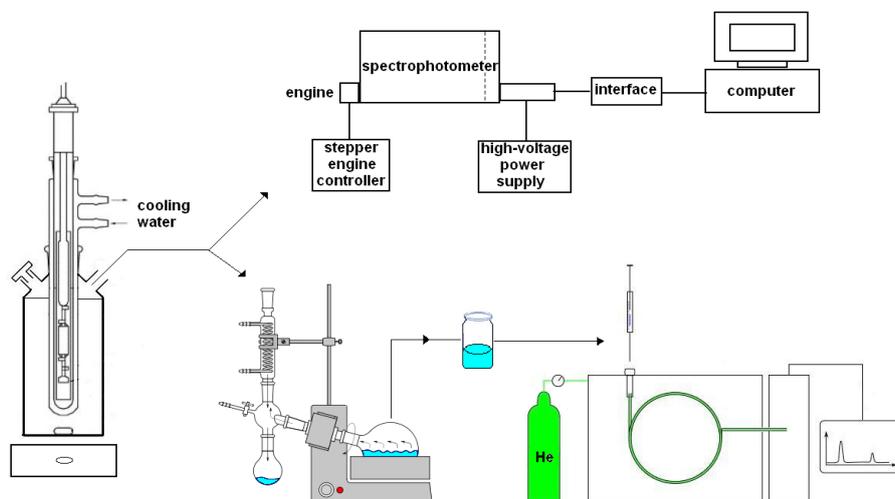


Figure 1. Schematic diagram of experimental procedures.

(SCRF) with the polarized continuum model (PCM) [22,23] and Bondi-type parameterization was used. All density functional theory (DFT) calculations presented here were performed using Gaussian 03 software [30]. Global reactivity indices, such as absolute electronegativity χ , hardness η [31], and electrophilicity ω [32] were calculated from the Eqs. 1-3:

$$\chi = -(E_{\text{LUMO}} + E_{\text{HOMO}})/2 \quad (1)$$

$$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}})/2 \quad (2)$$

$$\omega = \chi^2/2\eta \quad (3)$$

Energy of the lowest unoccupied molecular orbital, E_{LUMO} and the highest occupied molecular orbital, E_{HOMO} were calculated for the optimized at B3LYP/6-31+G(d,p) structures using the Møller-Plesset perturbation method [33-38] and 6-31+G(d,p) basis set (MP2/6-31+G(d,p)). In order to characterize aromaticity of the studied compounds, a harmonic oscillator model of aromaticity (HOMA) index [39,40] was calculated according to the following equation:

$$\text{HOMA} = 1 - (\alpha/N) \sum (R_{\text{opt}} - R_i)^2 \quad (4)$$

where N is the number of bonds in the aromatic ring while α and R_{opt} are constants depending on the type of bond (for C-C bond α is 257.7, and R_{opt} is 1.388 Å). The condensed Fukui function f_j^- was calculated from the Eq. 5 according to the procedure proposed by Yang and Mortier [41]:

$$f_j^- = q_j(N) - q_j(N-1) \quad (5)$$

where q is NBO charge population calculated at the UB3LYP/6-311++G(2d,2p) level while N denotes number of electrons in the optimized structure.

4. Results and discussion

4.1. Characterization of the reaction mixture

In order to examine the effect of oxidizing and chlorinating agents on EHMC photodegradation, the following model systems were prepared: EHMC; EHMC/H₂O₂; EHMC/H₂O₂/HCl. Spectrophotometric measurements showed that in non-irradiated solutions a decrease in absorbance at $\lambda_{\text{max}} = 310$ nm was very small. In case of the EHMC/H₂O₂ system the absorbance diminished by about 10% after 28 days while the presence of HCl slightly accelerated the EHMC degradation.

After 24 hours of irradiation of the EHMC solution without HCl and H₂O₂ the absorbance was reduced by about 24% (Fig. 2a). Addition of H₂O₂ significantly influenced the rate of EHMC photodegradation. After 10 hours of irradiation the absorbance decreased by half. As one can see from Fig. 2a, the highest rate of EHMC conversion was achieved in case of the EHMC/H₂O₂/HCl/UV system. When the molar ratio of the EHMC/H₂O₂/HCl system was 1:10:10 photodegradation was considerably faster than in other cases (Fig. 2b). The GC/MS analysis showed that the main reactions occurring in the EHMC/H₂O₂/UV system were trans-cis photoisomerisation and photolysis, which confirmed the presence of 2-ethylhexyl alcohol (EHA) and Z-EHMC in the reaction system (Fig. 3). Noteworthy, this is consistent with the results reported in earlier studies [12,42,43].

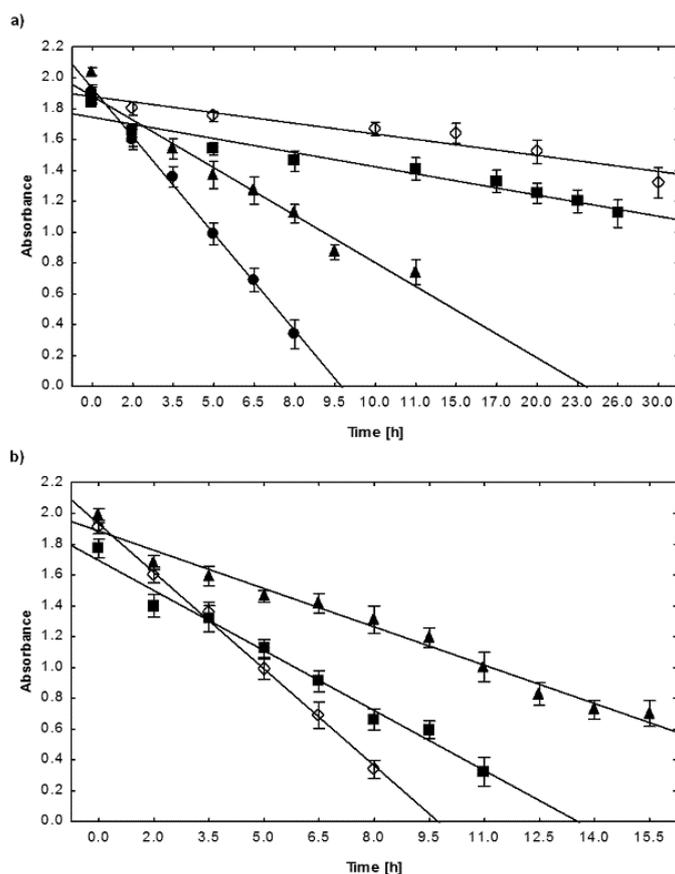


Figure 2. Changes in EHMC absorbance during UV irradiation: a) impact of the presence of H₂O₂ and HCl: —◇—EHMC, —■—EHMC/HCl [1:10], —▲—EHMC/H₂O₂ [1:10], —●—EHMC/H₂O₂/HCl [1:10:10], b) impact of molar ratio of EHMC/H₂O₂/HCl system: —◇— [1:10:10], —■— [1:10:5], —▲— [1:5:10].

Table 2. Mass spectral data of non-chlorinated compounds detected in all reaction mixtures and chloroorganic products detected in the EHMC/H₂O₂/HCl/UV system.

Compound	Abbreviation	Main m/z peaks (% of base peak)
2-ethylhexyl 4-methoxycinnamate	EHMC	178 (100), 161 (53), 134 (17), 133 (19)
2-ethylhexyl alcohol	EHA	83 (18), 70 (20), 57 (100), 41 (40)
4-methoxycinnamic acid	4-MCA	178 (100), 161 (37), 133 (22), 89 (18)
4-methoxybenzaldehyde	4-MBA	135 (100), 107 (12), 92 (19), 77 (38)
4-methoxyphenol	4-MP	124 (81), 109 (100), 81 (58), 53 (23)
3-chloro-4-methoxycinnamic acid	3-Cl-4-MCA	212 (100), 176 (55), 132 (38), 89 (23)
3,5-dichloro-4-methoxycinnamic acid	3,5-diCl-4-MCA	246 (100), 229 (46), 202 (32), 73 (21)
3-chloro-4-methoxybenzaldehyde	3-Cl-4-MBA	169 (100), 126 (11), 99 (18), 63 (25)
3,5-dichloro-4-methoxybenzaldehyde	3,5-diCl-4-MBA	203(100), 160 (60), 209 (10), 65 (20)
3-chloro-4-methoxyphenol	3-Cl-4-MP	158 (61), 143 (100), 107 (38), 55 (33)
2,5-dichloro-4-methoxyphenol	2,5-diCl-4-MP	192 (56), 177 (100), 149 (33), 53 (41)

The EHMC conversion significantly increased with the addition of HCl to the system (Fig. 2a). As one can see from Fig. 3, much more of photodegradation products were formed during EHMC UV irradiation in

the presence of chlorinating agents than in case of the EHMC/H₂O₂/UV system. The following chloroorganic compounds, 3-chloro-4-methoxybenzaldehyde (3-Cl-4-MBA), 3,5-dichloro-4-methoxybenzaldehyde

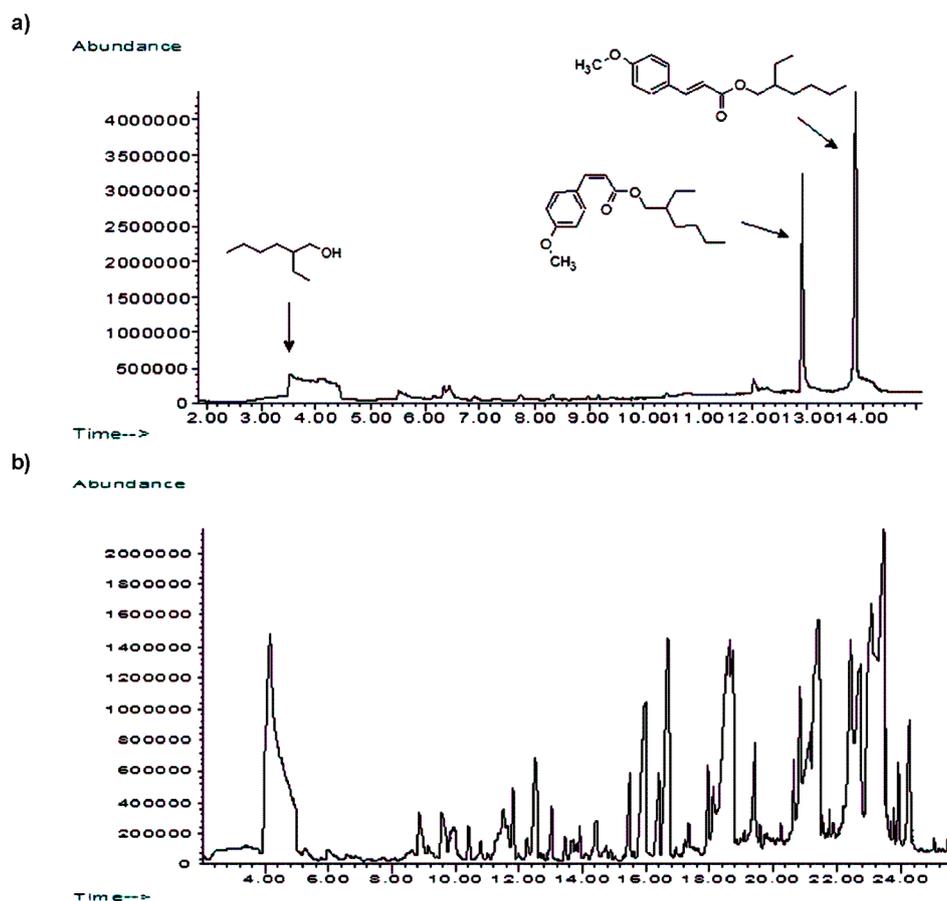


Figure 3. Gas chromatograms of the products of EHMC conversion in: a) EHMC/H₂O₂/UV [1:10] system and in b) EHMC/H₂O₂/HCl/UV system [1:10:10].

(3,5-diCl-4-MBA), 3-chloro-4-methoxyphenol (3-Cl-4-MP), 2,5-dichloro-4-methoxyphenol (2,5-diCl-4-MP), 3-chloro-4-methoxycinnamic acid (3-Cl-4-MCA), and 3,5-dichloro-4-methoxycinnamic acid (3,5-diCl-4-MCA) were identified in the reaction mixture (Table 2). Interestingly, we did not detect chloro-substituted EHMC derivatives. Based on the detected products in the EHMC/H₂O₂/UV and EHMC/H₂O₂/HCl/UV systems (Table 2), we proposed the following schematic pathways of EHMC photodegradation in the presence of ROCS (Fig. 4).

4.2. Thermodynamic insight into formation of detected products

Because the reaction proceeds very slowly without UV irradiation, the EHMC degradation is probably mainly photochemical and radical in nature. Photodissociation reactions of EHMC and H₂O₂ can be characterized by the bond dissociation enthalpy (BDE) defined as the enthalpy of reactions presented in Figs. 5a and 5b. According to the B3LYP/6-31+G(d,p) thermochemical calculations, the values of H₂O₂ and EHMC BDE are respectively

69.70 kcal mol⁻¹ and 44.20 kcal mol⁻¹, corresponding to 410.33 nm and 646.66 nm when expressed in wavelength. This shows that photodegradation reactions can occur under irradiation provided by the light source used in the experiment. It is worth noting that the C–O bond cleavage in the alkoxy moiety (BDE=117.60 kcal mol⁻¹) is less favorable than in case of the C–O bond cleavage between the carbonyl carbon and the alkoxy oxygen presented in Fig. 5a. 4-Methoxycinnamoyl radical formed via EHMC photolysis is probably further oxidized to 4-MCA, 4-MBA, and 4-MP. Although hydroxyl radicals are very short-lived species they are regarded as oxidizing agents in many photoinduced reactions between organic compounds and H₂O₂ [44-46]. As we found, ΔH and ΔG values of the reaction between 4-methoxycinnamoyl and $\cdot\text{OH}$ are -101.10 kcal mol⁻¹ and -89.59 kcal mol⁻¹, respectively. Highly favorable reaction with $\cdot\text{OH}$ is characteristic for antioxidants. It is worth mentioning that the growth of EHMC antioxidant activity during UV irradiation was experimentally proved by Dobashi *et al.* [1].

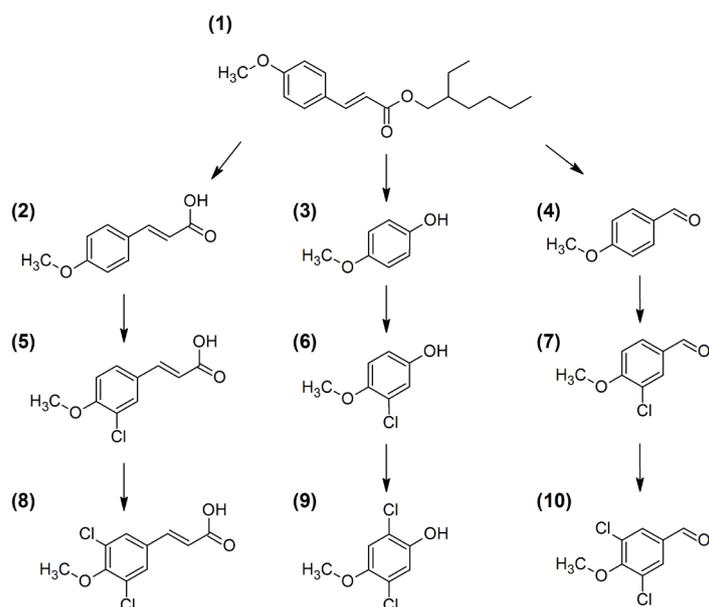


Figure 4. Proposed mechanistic pathways for EHMC photodegradation in presence of H_2O_2 and HCl ; (1) E-EHMC, (2) 4-MCA, (3) 4-MP, (4) 4-MBA, (5) 3-Cl-4-MCA, (6) 3-Cl-4-MP, (7) 3-Cl-4-MBA, (8) 3,5-diCl-4-MCA, (9) 2,5-diCl-4-MP, (10) 3,5-diCl-4-MBA.

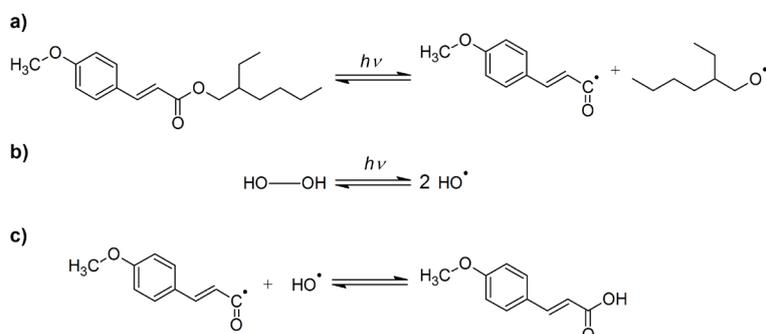


Figure 5. Radical reactions of EHMC and H_2O_2 occurring under the influence of UV light.

In order to evaluate which compounds are more favorable to form, the standard ΔH and ΔG of mono- and dichlorination reactions (Fig. 6) and negative logarithm of the equilibrium constant, $\text{p}K$, were analyzed (Table 3). Based on the approach presented by Li *et al.* [47], all of the available ring positions in 4-MCA, 4-MBA, and 4-MP were examined. It is well known that ΔG is a much better criterion of thermodynamic stability because it includes the entropy factor. Generally, the entropy contribution to the ΔG ($-\text{T}\Delta\text{S}$) is the most significant when $\text{R}=\text{OH}$ or Me and almost negligible when $\text{R}=\text{Ph}$ (Table 3). Nevertheless, a good correlation coefficient between the calculated values of ΔG and ΔH ($r=0.99$) indicates that both functions are equivalent in evaluating the thermodynamic stability of chloroorganic compounds.

$\text{H}_2\text{O}_2/\text{HCl}$ system is mainly a source of HOCl and Cl_2 . From the thermodynamic point of view HOCl is a more efficient chlorinating agent than Cl_2 (Table 3).

This is a general rule since the gas phase enthalpies of monochlorination of benzene with Cl_2 and HOCl , calculated from the experimental data [48–51], are $-28.85 \text{ kcal mol}^{-1}$ and $-46.79 \text{ kcal mol}^{-1}$ respectively. As one can see from Table 3, reactions of 4-MCA, 4-MBA, and 4-MP with Cl_2 and HOCl are in all cases exothermic ($\Delta\text{H}<0$) and favorable ($\Delta\text{G}<0$). However, the ΔH and ΔG values calculated for the isodesmic reactions (Fig. 6; $\text{R}=\text{Me}$, Ph) indicate that chlorination of 4-MCA, 4-MBA, and 4-MP is less favorable than chlorination of methane or benzene.

Mono- and dichlorinated 4-MCA, 4-MBA, and 4-MP derivatives can be classified into six categories: monochloro-4-methoxycinnamic acids (2-Cl-4-MCA and 3-Cl-4-MCA), dichloro-4-methoxycinnamic acids (2,3-diCl-4-MCA, 2,5-diCl-4-MCA, 2,6-diCl-4-MCA, 3,5-diCl-4-MCA), monochloro-4-methoxybenzenealdehydes (2-Cl-4-MBA, 3-Cl-4-MBA),

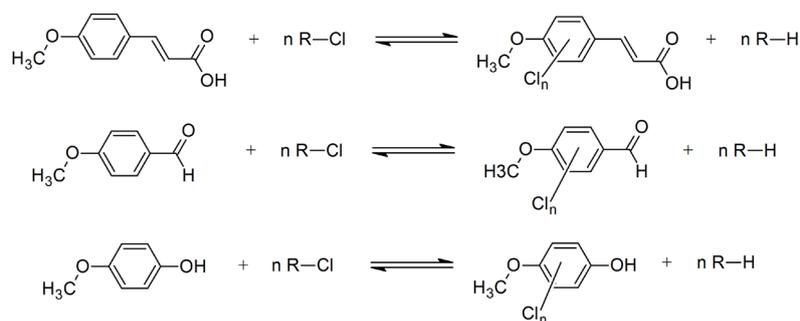


Figure 6. Theoretical reactions proposed for thermodynamic stability estimation of chloro-substituted compounds, R=Cl, OH, Me, Ph and n = 1, 2.

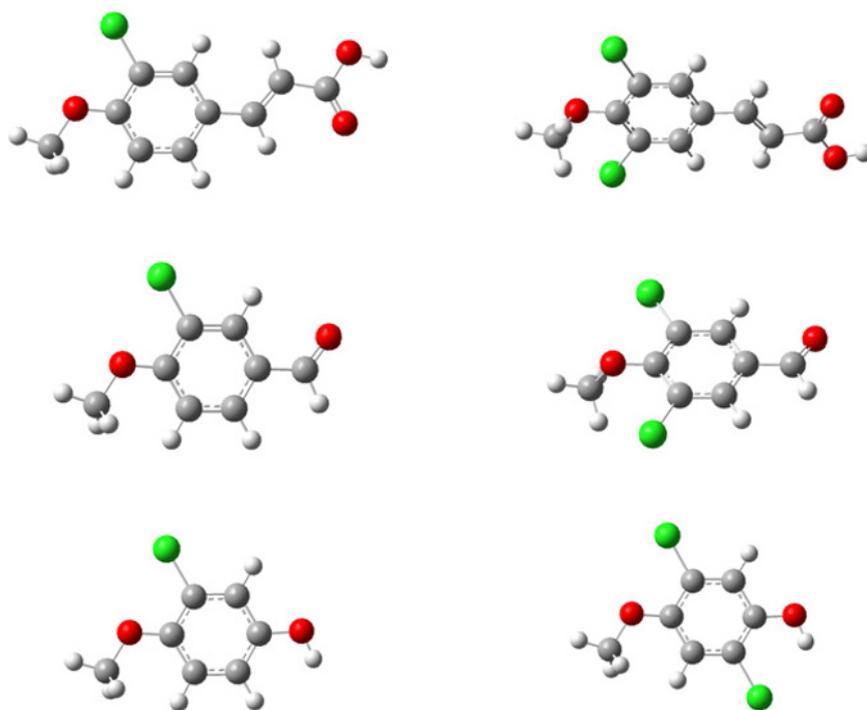


Figure 7. Visual representation of mono- and dichlorinated 4-MCA, 4-MBA and 4-MP derivatives detected in the EHM/H₂O₂/HCl/UV system.

dichloro-4-methoxybenzenealdehydes (2,3-diCl-4-MBA, 2,5-diCl-4-MBA, 2,6-diCl-4-MBA, 3,5-diCl-4-MBA), monochloro-4-methoxyphenols (2-Cl-4-MP, 3-Cl-4-MP), and dichloro-4-methoxyphenols (2,3-diCl-4-MP, 2,5-diCl-4-MP, 2,6-diCl-4-MP, 3,5-diCl-4-MP). When comparing two isomers, lower values of ΔH and ΔG indicate higher stability. As we found, chlorination reactions do not in all cases lead to the most thermodynamically favorable product. The most stable isomers were not detected among monochlorinated 4-MP, dichlorinated 4-MCA and 4-MBA derivatives. It is worth to note that in case of 4-MCA and 4-MBA the second chlorination occurs at sterically hindered sites (Fig. 7). Obviously, these pathways seem to be less thermodynamically favorable, which was confirmed by our calculations.

In our experiments the vicinal dichlorinated compounds were not detected in the reaction mixture. Obviously chlorination of 4-MCA and 4-MBA occurs according to the electron-donating resonance effect of the MeO substituent (+R) and the electron-withdrawing resonance effects of the CH=CHCOOH and CHO groups (-R). From the thermodynamic point of view formation of vicinal dichlorinated isomers, 2,3-diCl-4-MCA, 2,3-diCl-4-MBA and 2,3-diCl-4-MP is also less favorable than formation of 2,5-diCl-4-MP, 3,5-diCl-4-MBA and 3,5-diCl-4-MCA detected in the reaction mixture (Table 3). It is worth mentioning that DFT thermochemical calculations presented by Li *et al.* [47] demonstrated that the repulsion of the nearest chlorine atoms in a molecule is a destabilizing factor.

Table 3. Thermodynamic data calculated for monochlorination and dichlorination reactions shown in Fig. 6.

Product	R	ΔH (kcal mol ⁻¹)	ΔG (kcal mol ⁻¹)	pK	Product	R	ΔH (kcal mol ⁻¹)	ΔG (kcal mol ⁻¹)	pK
2-Cl-4-MCA	Cl	-30.15	-29.69	-21.78	2,5-diCl-4-MBA	Cl	-58.86	-57.85	-42.44
	OH	-45.05	-43.80	-32.13		OH	-88.65	-86.06	-63.13
	Me	1.43	2.73	2.00		Me	4.31	7.00	5.13
	Ph	3.17	3.17	2.33		Ph	7.78	7.88	5.78
3-Cl-4-MCA	Cl	-30.67	-29.98	-21.99	2,6-diCl-4-MBA	Cl	-50.59	-49.90	-36.60
	OH	-45.57	-44.08	-32.33		OH	-80.38	-78.11	-57.30
	Me	0.91	2.45	1.80		Me	12.58	14.95	10.97
	Ph	2.65	2.89	2.12		Ph	16.04	15.83	11.61
2,3-diCl-4-MCA	Cl	-57.17	-56.04	-41.11	3,5-diCl-4-MBA	Cl	-55.26	-54.95	-40.31
	OH	-86.96	-84.25	-61.8		OH	-85.06	-83.16	-61.00
	Me	6.00	8.81	6.46		Me	7.90	9.90	7.26
	Ph	9.47	9.69	7.11		Ph	11.37	10.78	7.91
2,5-diCl-4-MCA	Cl	-60.16	-58.99	-43.27	2-Cl-4-MP	Cl	-31.66	-31.29	-22.95
	OH	-89.95	-87.20	-63.96		OH	-46.55	-45.39	-33.30
	Me	3.00	5.85	4.29		Me	-0.08	1.14	0.84
	Ph	6.47	6.73	4.94		Ph	1.66	1.58	1.16
2,6-diCl-4-MCA	Cl	-56.63	-55.55	-40.75	3-Cl-4-MP	Cl	-31.06	-30.66	-22.49
	OH	-86.42	-83.76	-61.44		OH	-45.95	-44.77	-32.84
	Me	6.54	9.30	6.82		Me	0.53	1.76	1.29
	Ph	10.00	10.18	7.47		Ph	2.26	2.20	1.61
3,5-diCl-4-MCA	Cl	-50.10	-49.66	-36.43	2,3-diCl-4-MP	Cl	-59.47	-58.53	-42.93
	OH	-79.89	-77.87	-57.12		OH	-89.26	-86.74	-63.63
	Me	13.07	15.18	11.14		Me	3.70	6.32	4.64
	Ph	16.53	16.06	11.78		Ph	7.17	7.20	5.28
2-Cl-4-MBA	Cl	-29.29	-28.81	-21.13	2,5-diCl-4-MP	Cl	-61.94	-61.00	-44.75
	OH	-44.19	-42.92	-31.48		OH	-91.73	-89.21	-65.44
	Me	2.29	3.61	2.65		Me	1.23	3.84	2.82
	Ph	4.03	4.05	2.97		Ph	4.70	4.72	3.46
3-Cl-4-MBA	Cl	-30.25	-29.72	-21.80	2,6-diCl-4-MP	Cl	-61.79	-60.94	-44.70
	OH	-45.14	-43.83	-32.15		OH	-91.59	-89.15	-65.39
	Me	1.34	2.70	1.98		Me	1.37	3.91	2.87
	Ph	3.07	3.14	2.30		Ph	4.84	4.79	3.51
2,3-diCl-4-MBA	Cl	-56.04	-54.90	-40.27	3,5-diCl-4-MP	Cl	-59.24	-58.65	-43.02
	OH	-85.83	-83.11	-60.96		OH	-89.03	-86.86	-63.71
	Me	7.13	9.95	7.30		Me	3.94	6.02	4.42
	Ph	10.60	10.83	7.94		Ph	7.40	7.08	5.19

4.3. Reactivity indices and charge density analysis

It is well known that chemical species which are highly reactive are usually very unstable. Because of this fact,

stability of compounds can be measured in terms of reactivity indices [52]. It is important to note that aromatic systems are generally more stable than non-aromatic ones and hence aromaticity indices are often used in

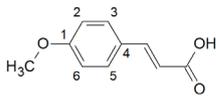
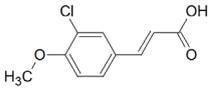
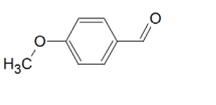
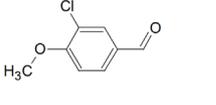
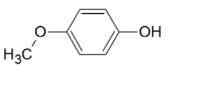
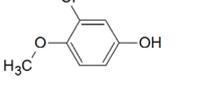
Table 4. Reactivity indices derived from HOMO and LUMO energy levels and benzene ring geometry.

Compound	HOMA	χ	η	ω
		[kcal mol ⁻¹]	[kcal mol ⁻¹]	[kcal mol ⁻¹]
EHMC	0.922	75.30	112.95	25.10
4-MCA	0.923	77.50	111.38	26.96
4-MBA	0.920	80.32	123.62	26.09
4-MP	0.966	68.71	119.54	19.75
2-Cl-4-MCA	0.917	81.26	111.38	29.64
3-Cl-4-MCA	0.919	79.69	112.32	28.27
2,3-diCl-4-MCA	0.906	82.83	111.7	30.71
2,5-diCl-4-MCA	0.913	83.14	112.01	30.86
2,6-diCl-4-MCA	0.911	87.22	115.46	32.95
3,5-diCl-4-MCA	0.940	82.83	116.09	29.55
2-Cl-4-MBA	0.916	85.03	122.68	29.47
3-Cl-4-MBA	0.917	83.14	123.93	27.89
2,3-diCl-4-MBA	0.910	87.22	122.36	31.09
2,5-diCl-4-MBA	0.915	87.22	122.36	31.09
2,6-diCl-4-MBA	0.895	88.48	124.25	31.50
3,5-diCl-4-MBA	0.945	92.56	126.44	33.88
2-Cl-4-MP	0.966	73.10	118.91	22.47
3-Cl-4-MP	0.964	72.48	119.54	21.97
2,3-diCl-4-MP	0.955	75.61	118.91	24.04
2,5-diCl-4-MP	0.964	74.99	120.17	23.40
2,6-diCl-4-MP	0.965	77.18	118.60	25.12
3,5-diCl-4-MP	0.966	79.38	123.93	25.42

evaluation of reactivity and stability [40,53]. Generally, chlorinated 4-MCA, 4-MBA and 4-MP isomers which are more aromatic and which exhibit higher hardness than others were formed under the experimental conditions (Table 4). However, in case of monochlorinated 4-MP derivatives, 3-Cl-4-MP, not 2-Cl-4-MP, was detected (Fig. 4) although 2-Cl-4-MP is slightly more aromatic.

As might be expected, the introduction of a chlorine atom into the molecule results in an increase of electronegativity. It means that monochlorinated 4-MCA, 4-MBA and 4-MP are probably less nucleophilic than non-chlorinated ones. Generally speaking the second chlorination step is often kinetically less favorable than the first step. For instance, electrophilic chlorination of benzene using the FeCl₃/PhNO₂ system is several times faster than in the case of chlorobenzene [54]. According to the Hammond postulate [55] reaction intermediates are energetically close to the transition states, which means that the formation of stable σ -complexes

Table 5. NBO charges and Fukui function f_j^- values in EHMC, 4-MCA, 4-MBA, 4-MP, 3-Cl-4-MCA, 3-Cl-4-MBA and 3-Cl-4-MP.

Compound	Position	NBO Charges	f_j^-
	1	0.341	0.13
	2	-0.294	0.10
	3	-0.191	0.00
	4	-0.144	0.22
	5	-0.184	0.03
	6	-0.324	0.06
	1	0.334	0.13
	2	-0.095	0.08
	3	-0.202	0.00
	4	-0.126	0.20
	5	-0.182	0.05
	6	-0.314	0.06
	1	0.359	0.12
	2	-0.290	0.14
	3	-0.180	0.00
	4	-0.223	0.27
	5	-0.167	0.00
	6	-0.335	0.14
	1	0.334	0.12
	2	-0.095	0.16
	3	-0.202	0.00
	4	-0.126	0.23
	5	-0.128	0.02
	6	-0.314	0.07
	1	0.281	0.17
	2	-0.278	0.08
	3	-0.303	0.03
	4	0.273	0.19
	5	-0.290	0.08
	6	-0.314	0.06
	1	0.276	0.17
	2	-0.084	0.07
	3	-0.297	0.02
	4	0.290	0.17
	5	-0.300	0.10
	6	-0.296	0.04

is kinetically advantageous. Obviously, the charge density on carbon atoms determines the stability of the σ -complexes with electrophiles. One of the useful methods for evaluating susceptibility of certain atoms in a molecule to either nucleophilic or electrophilic attack is

a charge distribution analysis [56–60]. Our calculations demonstrated that chlorination occurs at the atoms with the highest electron density (Table 5). This is consistent with the resonance effects of the substituents attached to the benzene ring. In case of 4-MCA and 4-MBA the electron-donating methoxyl group (MeO) is conjugated with the electron-withdrawing substituent, CH=CHCOOH and CHO respectively. The substituent constants σ_p^- of MeO, CH=CHCOOH, and CHO groups are -0.26, 0.62, and 1.03 respectively [61]. This shows that C-2 and C-6 atoms (numeration according to Table 5) in 4-MCA and 4-MBA are the most susceptible to substitution by the chlorinating agent. From the local reactivity point of view nucleophilicity of particular atoms in the molecule can be evaluated by means of the Fukui function f_j^- . As we found, chlorination reactions occur at the atoms with the highest values of f_j^- among all sites available for substitution. As it can be expected, the electrophilic attack of a chlorinating agent is, in case of 3-Cl-4-MP, the most probable at C-5 atom. This is of course determined by the electron-donating resonance effects (+R) of the OH and Cl groups attached to the benzene ring (σ_R of OH and Cl substituents are -0.43 and -0.16 respectively [61]). Besides, the calculated f_j^- values also indicate that C-5 atom is more nucleophilic than C-3 or C-6.

5. Conclusions

In this study we examined the effect of common oxidizing and chlorinating agents on EHMC photodegradation.

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Experimental data demonstrated that EHMC photostability decreases in the presence of ROCS. Spectrophotometric measurements indicated that the reaction proceeds very slowly without UV irradiation. This shows that EHMC is relatively stable in the presence of ROCS when photolysis efficiency is reduced.

The mechanism of 4-MCA, 4-MBA, and 4-MP chlorination is probably complex and consists of radical and ionic steps, including photoinduced C–O bond cleavage, oxidation, and chlorination. DFT thermochemical calculations demonstrated that reactions of 4-MCA, 4-MBA, and 4-MP with Cl_2 and HOCl are in all cases thermodynamically probable ($\Delta G < 0$) and exothermic ($\Delta H < 0$). However, the thermodynamic analysis does not provide a sufficient explanation of chloroorganic compounds formation. In most cases chlorinated 4-MCA, 4-MBA, and 4-MP isomers, which are “harder” than others, were identified in the reaction mixture. This is consistent with the “Maximum Hardness Principle”, according to which stable chemical species are less polarizable than unstable ones [52]. In order to better understand the mechanism of formation of chloroorganic compounds the local nucleophilicity was described by means of the Fukui function.

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