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Photocatalytic oxidation of the herbicide (4-chloro-2-methylphenoxy)acetic acid (MCPA) over TiO$_2$

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Abstract

The photocatalytic decomposition of the herbicide (4-chloro-2-methylphenoxy)acetic acid (MCPA), C$_9$H$_9$ClO$_3$, in aqueous suspensions containing TiO$_2$ was investigated by following the formation of intermediates via recording proton NMR spectra. One of theoretically possible intermediates, 4-chloro-2-methylphenolmethanoate, was synthesized by a modified esterification procedure. Based on the data obtained a possible reaction mechanism was proposed. The rate of MCPA aromatic ring decomposition was followed by pH changes during illumination. As a result, apparent reaction rate constant was found to be 7.0×10^{-6} mol dm^{-3} min^{-1}. The complete mineralization was attained after about 15 h of illumination. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalytic oxidation; Herbicide MCPA; Titanium(IV) oxide

1. Introduction

The photoexcitation of TiO$_2$ taking place under irradiation with light of suitable wavelength, generates an electron−hole pair, creating the potential for both reduction and oxidation processes to occur at the surface of the semiconductor for nearly all substrates investigated [1]. Although a number of possible degradation pathways can be envisioned, the formation and subsequent reactions of hydroxyl radicals, being a very strong oxidizing agent (standard redox potential +2.8 V [2]), generated from the oxidation of water molecules and OH$^-$ ions by photoexcited TiO$_2$, are generally accepted as the predominant degradation pathways of organic substrates in oxygenated aqueous solutions. In this way, in particular, halogenated compounds (alkanes, alkenes and aromatic compounds) were reported to undergo complete mineralization in water suspensions of TiO$_2$, with the formation of CO$_2$, H$_2$O and mineral acids [3].

In this study, the herbicide (4-chloro-2-methylphenoxy)-acetic acid (MCPA) was chosen as a model compound of an organic waste photodegradable substance in water in view of its wide use all over the world. As reported in [4], it is one of the pesticides that is most frequently found in drinking water. Continuing on our investigations [5], in the present work we studied the photocatalytic decomposition

of MCPA, present at low concentrations in aqueous suspensions of TiO$_2$, as well as the nature of intermediates formed, by NMR measurements. On the basis of the obtained data we suggested a probable decomposition mechanism. Based on the pH changes during illumination the probable kinetics of MCPA aromatic ring degradation was proposed.

2. Experimental

The herbicide MCPA, C$_9$H$_9$ClO$_3$ (98.8% purity), purchased from Riedel-de Haen, was used without further purification.

All the experiments were carried out using 2 mg cm^{-3} suspensions of TiO$_2$ (Degussa P-25). Solutions were prepared in D$_2$O for NMR measurements. Suspensions of TiO$_2$ containing MCPA (3 mmol dm^{-3}) were sonicated for 15 min before illumination, to make the TiO$_2$ particles uniform. The photochemical cell (sample volume 20 cm^3) was made of Pyrex glass with a plain window (on which the light beam was focused), equipped with a magnetic stirring bar, a water circulating jacket, and two openings: for O$_2$ stream and taking of NMR sample (volume 0.5 cm^3). The process was carried out at temperature of $43 \pm 1°$C. A 125 W mercury lamp (Philips, HPL-N) was employed as the radiation source. The proton NMR spectral profiles were monitored on a Bruker AC-250 instrument after increasing illumination times in the presence of TiO$_2$ particles. The same instrument

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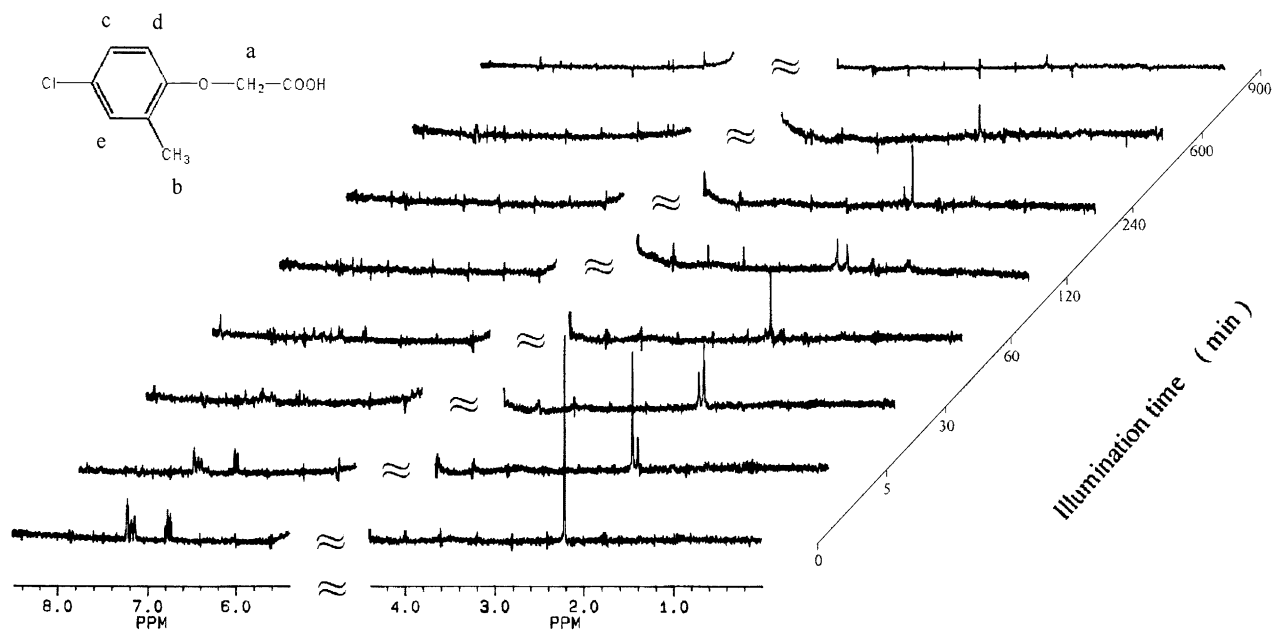*E-mail address:* andjelka@ih.ns.ac.yu (A. Topalov).

Fig. 1. Temporal ^{1}H NMR spectral profiles during the photooxidative decomposition of MCPA in D_2O solution (3.0 mmol dm^{-3}) in the presence of TiO_2 (2 mg cm^{-3}).
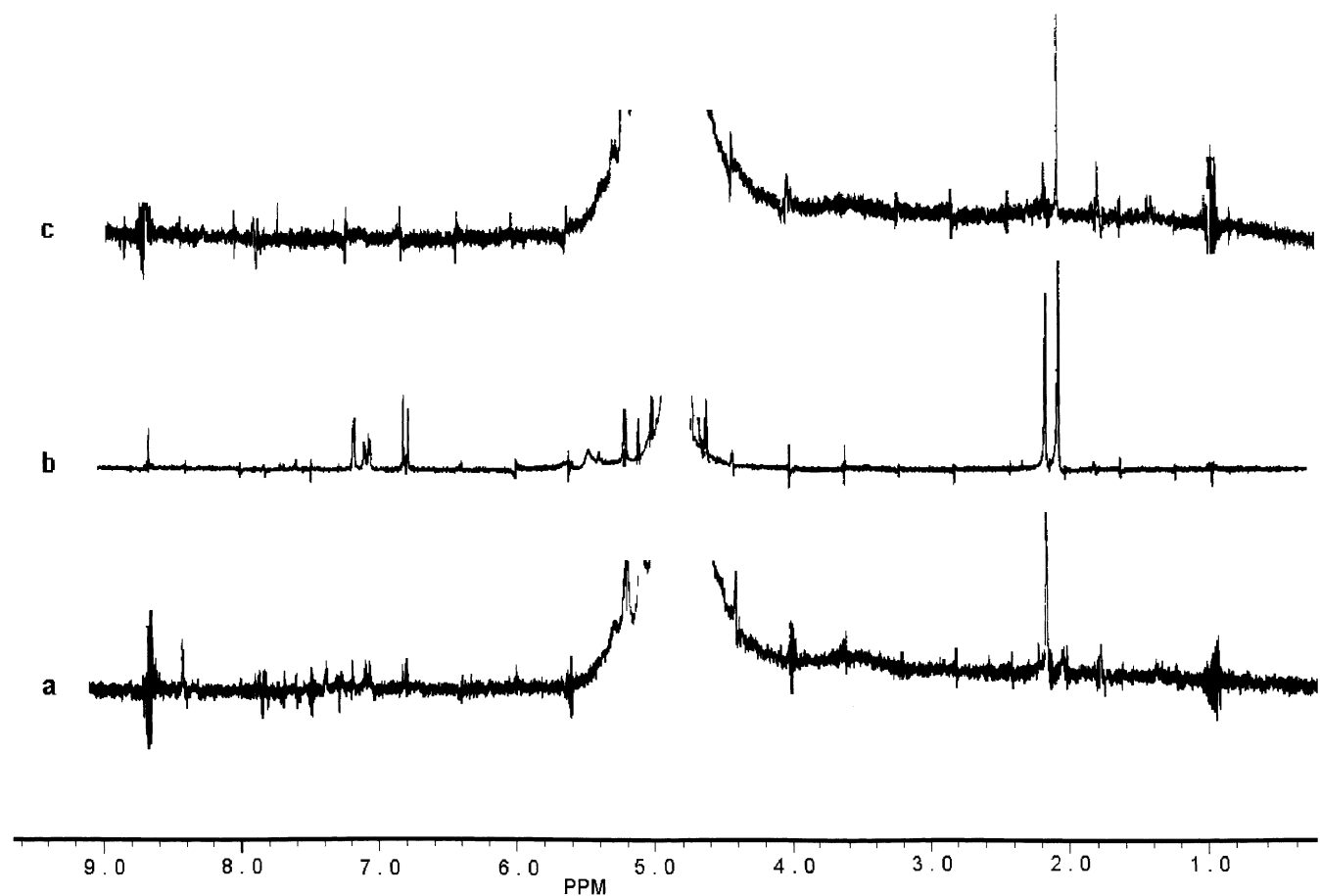

Fig. 2. ^{1}H NMR spectra: (a) MCPA after 60 min of illumination; (b) mixture of 4-chloro-2-methylphenol and acetic acid; (c) MCPA after 240 min of illumination.

was used to record the ^{13}C NMR spectra. The ^{1}H chemical shifts were referred to the 3-trimethylsilyl-1-propane sulfonic acid, sodium salt (DSS) signal.

One of theoretically possible intermediates, 4-chloro-2-methylphenylmethanoate, was synthesized by a modified esterification procedure [6]. The amount of 1.37 mmol of 4-chloro-2-methylphenol (Aldrich, purity 97%) was dissolved in 15.6 mmol of formic acid (Kemika, p.a., purity 98–100%) with 1.73 mmol of phosphorous(V) oxide (Merck, purity 98%). The reaction mixture was held 3 days at room temperature, protected from air and light, and after that it was poured into the mixture of 50 cm^3 of water and 10 cm^3 of diethyl ether. The pH value of this mixture (7.5–8.0) was maintained with solid sodium hydrogencarbonate. The mixture was extracted with 3 × 10 cm^3 of diethyl ether. The organic phase was dried over anhydrous sodium sulfate and then filtered. The filtrate was evaporated under reduced pressure to yield 0.25 g of crude product as brown oil. The crude product was purified on column of 10.0 g of silica gel and eluted with toluene. After evaporation under reduced pressure, the quantity of 0.20 g of 4-chloro-2-methylphenylmethanoate was obtained as light yellow oil (85%) with ^{1}H NMR [CDCl$_3$, δ (ppm)]: 2.21 (3H, s, CH$_3$); 7.02 (1H, d, $J_{5,6} = 8.5$ Hz, aromatic H-6); 7.21 (1H, dd, $J_{5,6} = 8.5$ Hz, $J_{5,3} = 2.6$ Hz, aromatic H-5); 7.26 (1H, d, $J_{5,3} = 2.6$ Hz, aromatic H-3); 8.30 (1H, s, OC$\underline{H}$O) and ^{13}C NMR [CDCl$_3$, δ (ppm)]: 158.6 (O$\underline{C}$HO); 146.8 (C$_q$); 131.8 (C$_q$); 131.6 (C$_q$); 131.1 (CH); 127.0 (CH); 122.8 (CH); 16.2 (CH$_3$).

Under the same conditions, as for NMR measurements, except of using double-distilled water, the change of pH values during the MCPA photodegradation was measured continuously with the aid of a combined glass electrode (Iskra) connected to a pH-meter (Iskra MA 5706). Kinetic curves were recorded by means of a chart recorder (Goerz–Electro Servogor Sb RE 647.9).

3. Results and discussion

The photoassisted oxidative degradation of MCPA in the presence of TiO$_2$ involves formation of a variety of intermediate species, whose temporal ^{1}H NMR spectra are presented in Fig. 1. The ^{1}H NMR signals [D$_2$O, δ (ppm)] of parent substance were: 2.21 (3H, s, CH$_3$) (**b**); 6.75 (1H, d, $J_{5,6} = 8.6$ Hz, aromatic proton) (**d**); 7.15 (1H, dd, $J_{5,6} = 8.6$ Hz, $J_{3,5} \sim 1$ Hz, aromatic proton) (**c**); 7.22 (1H, d, $J_{3,5} \sim 1$ Hz, aromatic proton) (**e**). The signals of methylene protons (O–CH$_2$–) in the position (**a**) were overlapped by the HDO signal from D$_2$O, which hindered their monitoring during the degradation process. During the illumination, the signals of parent substance showed an abrupt decrease and after 60 min of illumination they disappeared. After only 5 min of illumination, new signals of the degradation product there appeared: singlet at 2.17 ppm (belonging to CH$_3$) and three signals in the range of
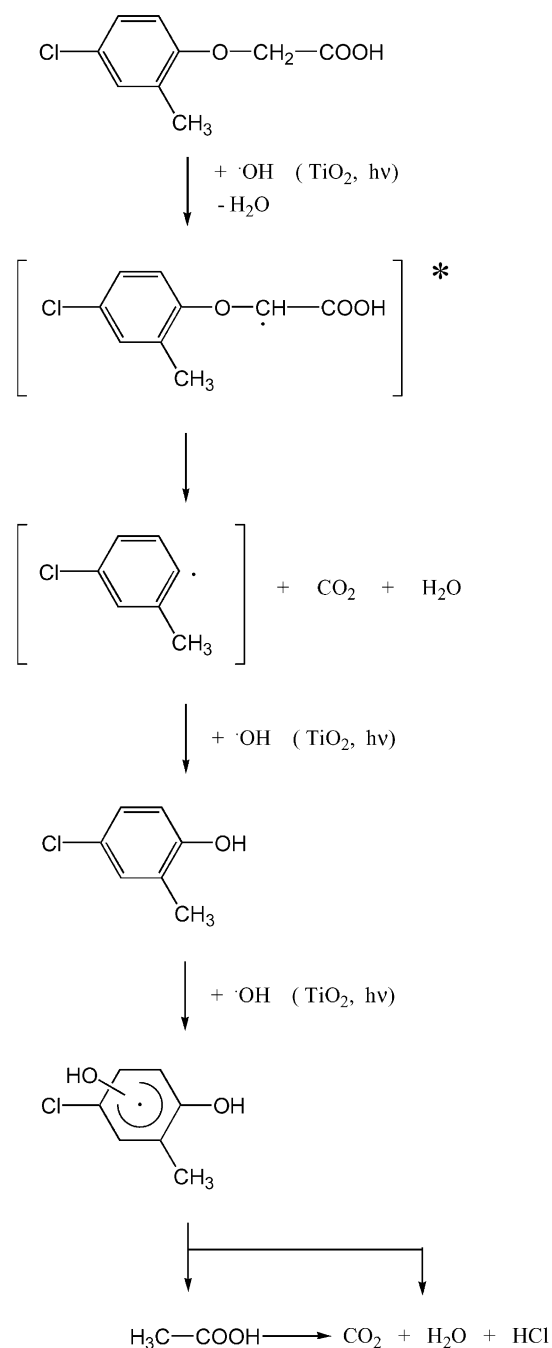

Fig. 3. Possible pathway of MCPA photodegradation in the presence of TiO$_2$.

7.0–8.0 ppm (belonging to aromatic protons). These signals can be ascribed to 4-chloro-2-methylphenol which was confirmed by adding this compound and comparing its ^{1}H NMR spectrum with the spectrum of the MCPA decomposition products present after 60 min of illumination (Fig. 2a and b). They reach a maximum between 30 and 60 min, then show a decrease, being the only degradation product after 60 min, and to disappear almost completely after 240 min. After 120 min of illumination, the new singlet at 2.07 ppm
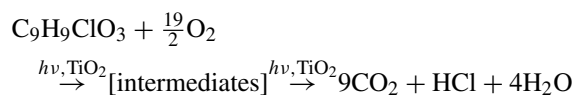
appeared belonging to CH_3 group, originated from acetic acid. This was confirmed by comparing the ^1H NMR spectra of acetic acid and that of the MCPA decomposition products resulting after 240 min of illumination (Fig. 2b and c). In the beginning, this signal was of a comparable intensity to the signals of the other intermediate, showing a sharp increase after that, reaching a maximum after 240 min, being the only degradation product after 600 min, and hardly visible after 900 min.

At the beginning of irradiation the MCPA existed predominantly in the form of molecules because the calculated degree of ionization was about 30% ($pK = 3.39$, determined from the pH value measured at the beginning of degradation and from initial concentration of MCPA $= 3.0\,mmol\,dm^{-3}$). In view of the fact that the investigated solution contained ionic form of MCPA it could be postulated the formation of 4-chloro-2-methylphenylmethanoate as intermediate. This compound can be formed at the semiconductor surface by a direct hole oxidation of the tightly bound electron donor [7], such as the ionic form of MCPA molecule, followed by reactions with hydroxyl radicals. However, the presence of the proposed intermediate, 4-chloro-2-methylphenylmethanoate, could not be proved. Taking into account that we used D_2O as solvent, OD radicals were formed as active oxygen species [8]. We suppose that the degradation of the parent MCPA molecule yields the formation of 4-chloro-2-methylphenol, by elimination of CO_2 and H_2O. Further transformations of the aromatic ring is possible by the chlorine substitution with hydroxyl group, or by electrophilic addition of the OH radical. As a result of degradation of the aromatic part of the MCPA molecule, acetic acid is formed. By further action of OH radicals, acetic acid is decomposed into CO_2 and H_2O. The proposed pathway of hydroxylation of the aromatic ring and chloride evolution is in accordance with the observations of Mylonas and Papaconstantinou [9], Mylonas et al. [10], and Theurich et al. [11], who mentioned that OH radicals, as the main oxidant attacking the substrate, caused

hydroxylation products, and finally the opening of the ring. Our ^1H NMR spectra show that at the end of photodegradation (after about 15 h of illumination) there was no signal at 2.07 ppm, indicating that all acetic acid was transformed into CO_2 and H_2O.

Taking into account the nature of some of the observed species and the rate of their disappearance, as well as the data in [11–15], we proposed a probable scheme of MCPA degradation (Fig. 3). The analysis of the intermediates is based on the common tabular values of chemical shifts and coupling constants for the pertinent compounds, as discussed in our previous papers, in the case of the fungicide metalaxyl [16] and herbicide mecoprop [5].

The results obtained by studying the photocatalytic decomposition of various chlorine-containing compounds [5,17] show that, the complete degradation gives carbon dioxide, water, and hydrochloric acid. In the case of the MCPA photocatalytic degradation the overall stoichiometric reaction can be described as

$$C_9H_9ClO_3 + \frac{19}{2}O_2$$
$$\overset{hv,\,TiO_2}{\rightarrow} [\text{intermediates}] \overset{hv,\,TiO_2}{\rightarrow} 9CO_2 + HCl + 4H_2O$$

For this reason we decided to follow the photooxidation of MCPA by measuring the H^+ produced as a function of illumination time. The generation of H^+ during photolysis of MCPA is illustrated in Fig. 4. The maximal pH value obtained between 30 and 60 min of illumination can be attributed to the formation of less acidic intermediates compared to MCPA. The subsequent pH decrease, occurring at about 7 h, can be ascribed to the prevailing HCl release, the minimal value (pH 2.54) corresponding to the stoichiometric quantity of the acid evolved from MCPA. The data in [17] show that the photodecomposition of the aromatic ring with chlorine as substituent takes place simultaneously with the HCl evolution. So, in our case, the decreases in pH, after the maximum is attained, can be used to calculate
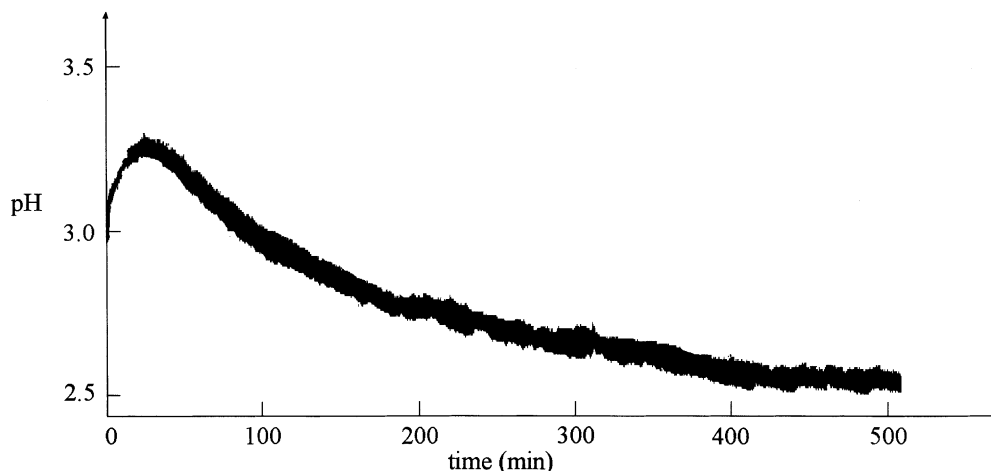

Fig. 4. Change of pH in photolysis of MCPA ($3.0\,mmol\,dm^{-3}$) in the presence of TiO_2 ($2\,mg\,cm^{-3}$).
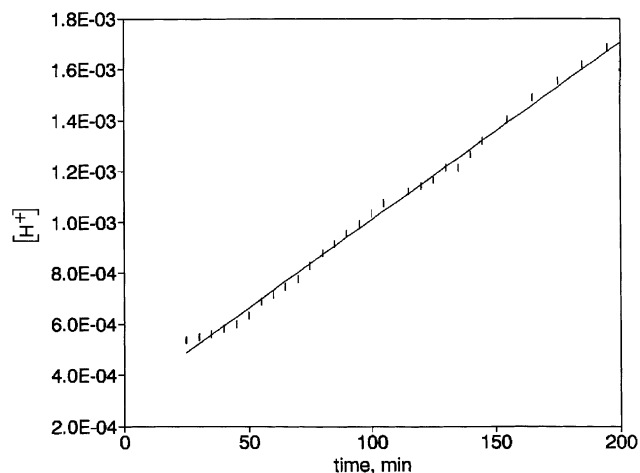
Fig. 5. The kinetics of the photodecomposition of MCPA aromatic ring.

the rate of photodecomposition of the aromatic ring. However, the effects of the other acidic intermediates should not be neglected [11]. The zero-order kinetics (agreeing well with the data in [11]) is observed (Fig. 5) with the average value for the apparent reaction rate constant $k_a = 7.0 \times 10^{-6}\,\mathrm{mol\,dm^{-3}\,min^{-1}}$ ($r = 0.998$).

In contrast to the herbicide mecoprop, $C_{10}H_{11}ClO_3$, which is decomposed in 30 min [5], the degradation of MCPA is completed in about 60 min, whereas a longer time is needed for intermediate decomposition of both pesticides. Taking into account that the mecoprop has one CH_3 group in the position (**a**), easier degradation of this herbicide can be expected, because of the formation of the thermodynamically favored tertiary alkyl radical in the first stage of decomposition [5]. In the case of MCPA, the formation of the possible radical in this stage is marked with an asterisk (Fig. 3), for which is needed a higher activation energy than for the mentioned mecoprop radical.

Finally, it can be concluded that TiO_2 photocatalysis is an extremely efficient method for elimination of the chlorine-containing organic contaminants from water.

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