

Reductive transformations of halophenols on illuminated ferrocyanide ions

Paola Calza, Valter Maurino, Ezio Pelizzetti*

Università di Torino, Dipartimento di Chimica Analitica, via P. Giuria 5, 10125 Torino, Italy

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Abstract

The reductive decomposition of several halogenated pollutants (2,4,5-trichlorophenol, 2,5 and 3,4-dichlorophenol, 2- and 4-chlorophenol, 4-bromophenol and 4-fluorophenol) was evaluated by adopting illuminated ferrocyanide ions as source for hydrated electrons; in these conditions, the photogenerated solvated electrons interact with substances present in solution so reducing them.

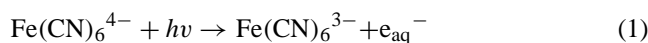
The constant rates of halophenols with hydrated electrons achieved with ferrocyanide system show a good correlation with the data estimated by adopting pulse radiolysis, so that it could be adopted as an alternative to the pulse radiolysis in evaluating the reactivity of organic compounds toward hydrated electrons. Furthermore, it permits to pursue the fate of initial molecule through the intermediates identification. As an example, a detailed study about the intermediates produced from 3,4-dichlorophenol and 2,4,5-trichlorophenol is presented and a pattern of reaction pathways accounting for the recognized intermediates is proposed.

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1. Introduction

Recently, reductive processes have attracted attention for the remedy of contaminated environments and have been proposed for pollutants abatement [1–6]. In the present work, we have employed illuminated ferrocyanide ions to produce hydrated electrons. The particular choice of irradiated ferrocyanide ions is due to its efficient electron injection process that undergoes upon light-excitation [7]. When an aqueous solution containing $\text{Fe}(\text{CN})_6^{4-}$ is irradiated with light at $\lambda < 350 \text{ nm}$, the following reaction occurs:



leading to the generation of hydrated electrons. Besides, the ferrocyanide system has the advantage to form a single reactive radical (i.e. the hydrated electrons) [8]. The only additional primary process known to take place in parallel to the electron generation is the formation of the aquapentacyanoferrite complex [9].

This system could be able to estimate the reaction rate of the organic compounds with hydrated electrons and it had already been successfully used in the studies on the

chloromethanes photoreduction [10]. Their rates of disappearance will be compared, when are available, with those obtained with pulse radiolysis, which is the technique commonly adopted in estimating the reaction rate with electrons. An interesting class of organic compound is represented by halophenols, for which the reactivity toward hydrated electrons is strongly dependent on the nature of halide atom, as assessed by pulse radiolysis quoted rates [11].

Even if halophenols decomposition has been widely studied employing heterogeneous photocatalytic system [12–17], photoinduced reactions [18,19], reaction with metals [20], radiolytic degradation [21,22] and bacteria [23], for polychlorophenols there are no literature data available about the reactions rate with hydrated electrons; in these cases, the ferrocyanide system could represent an alternative technique for their estimation.

It is of particular concern to identify the transformation products formed from the halophenols degradation and to assess their stability and toxicity, that could be even higher than the original molecule. Ferrocyanide system allows to appraise not only the reaction rate with electrons, but also to determine and quantify the intermediates arising during the reductive process. In the studies with pulse radiolysis, few investigations on the reaction products are available, so that the ferrocyanide system could be adopted as a complemen-

* Corresponding author. Tel.: +39-011-6707630;

fax: +39-011-6707615.

E-mail address: ezio.pelizzetti@unito.it (E. Pelizzetti).

tary technique representing a good tool for investigations in steady-state conditions.

2. Experimental

2.1. Material and reagents

2,4,5-Trichlorophenol (Aldrich), 3,4-dichlorophenol (Aldrich), 2,5-dichlorophenol (Aldrich), 2-chlorophenol (Aldrich), 4-chlorophenol (Aldrich), 4-bromophenol (Aldrich), 4-fluorophenol (Aldrich), and potassium ferrocyanide (Carlo Erba) were used as received. Sodium chloride (Merck), sodium fluoride (Merck) and potassium bromide (Merck) were used after drying.

2.2. Irradiation procedures

Irradiation were carried out on 5 ml of solution containing 20 mg L^{-1} halophenols and $\text{Fe}(\text{CN})_6^{4-} 1 \times 10^{-3} \text{ M}$, using a 1500 W Xenon lamp (Solarbox, CO. FO. MEGRA, Milan, Italy) simulating AM1 solar light and equipped with a 310 nm cut-off filter. The total photonic flux (310–400 nm) in the cell and the temperature have been kept constant for all the experiments. They were $7.9 \times 10^{-6} \text{ einstein min}^{-1}$ and 50°C , respectively.

Experiments were run at pH 7 and 11 (after adjustment with NaOH). The experiments under anaerobic conditions were prepared by purging with nitrogen for 30 min the irradiation cells filled with the solution except the organic compound. Following this procedure, the required volume of substrate stock solution was injected into the cell.

2.3. Analytical procedures

The contents of the cell were analysed by the appropriate analytical technique. The disappearance of the primary compound and the intermediates evolution with time were followed using high performance liquid chromatography (HPLC). A Rheodyne injector, a RP C18 column (Lichrochart, Merck, $12.5 \text{ cm} \times 0.4 \text{ cm}$, $5 \mu\text{m}$ packing), a high pressure two-pumps gradient (Merck Hitachi L-6200 and L-6000 pumps) and UV-Vis detection (Merck Hitachi L-4200) were used. The halophenols were analysed by utilizing a mixture of phosphate buffer and acetonitrile in ratio 60:40; under the reported condition, the retention times were: 11.8 min 2,4,5-trichlorophenol, 7.5 min 3,4-dichlorophenol, 7.9 min 3,5-dichlorophenol, 3.9 min 2-chlorophenol, 4.3 min 4-chlorophenol, 4.6 min 3-chlorophenol, 2.6 min phenol, 3.8 min 4-chlororesorcinol, 2.1 min resorcinol, 2.8 min 4-fluorophenol, 4.1 min 4-bromophenol.

A Dionex DX 500 apparatus equipped with a ED40 electrochemical detector and a GP40 gradient pump and a AS9HC anionic column was used for the analysis utilizing an alkaline buffer eluant containing NaHCO_3 (5 mM) and

Na_2CO_3 (12 mM) at the flow rate of 1 ml min^{-1} ; under these conditions, the retention time of fluoride, chloride and bromide were 3.7, 6.2 and 9.8 min, respectively.

An Agilent 6890 gaschromatograph equipped with an Agilent 5973 MS detector and a 19091S-433 HP-5MS ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) column was adopted for the identification of condensation products and the confirmation of the benzenes intermediates. The mass range is from 50 to 400 amu, the GC temperatures program is: initial hold for 2 min at 40°C , 8°C/min from 40 to 300°C and finally hold at 300°C for 5 min. In these conditions, the retention times are: 10.3 min for phenol, 14.1 min for 4-chlorophenol, 16.0 min for 4-chlororesorcinol, 17.2 min for 3,4-dichlorophenol, 26.3 min for 4,4'-dichloro-3-hydroxybiphenyl and 19.5 min for 4,4'-dichlorobiphenyl.

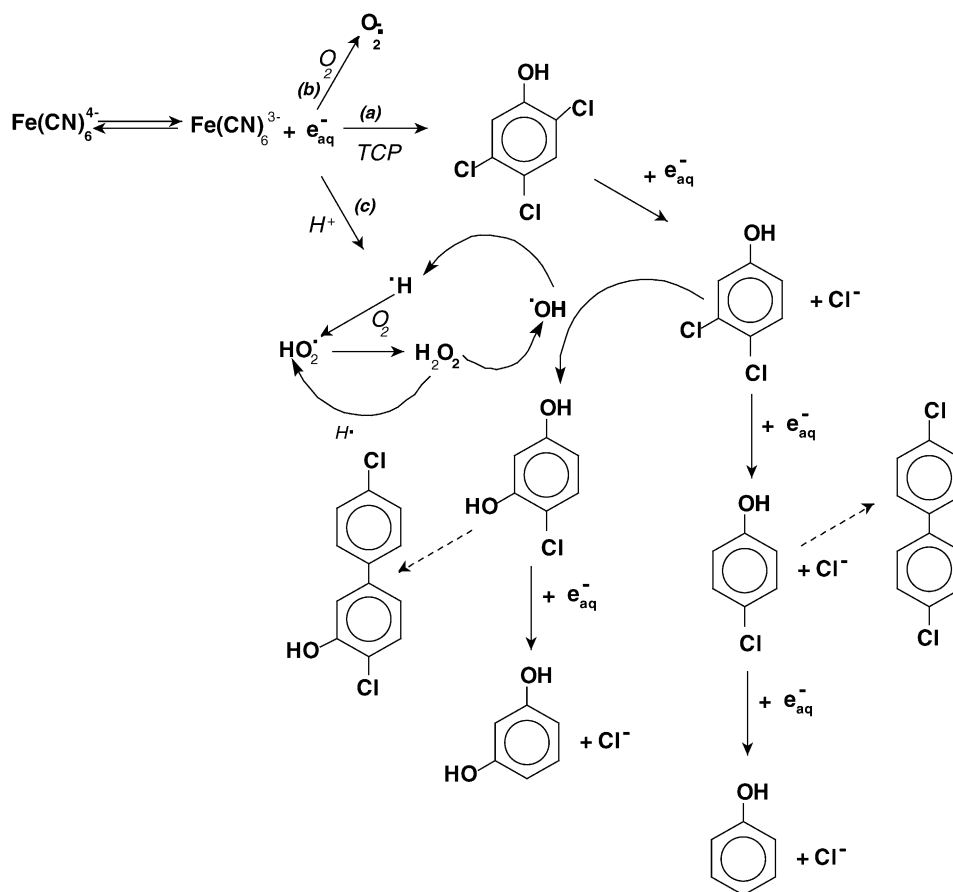
3. Results and discussion

The efficiency of hydrated electrons production, created through the reaction (1), could be modified by the occurrence of competitive reactions; in order to minimize them, it is necessary to carefully choose the experimental conditions. The main competitive reactions involving hydrated electrons are summarized in Scheme 1, where three main pathways can be recognized. The first one, indicated as *pathway a*, represents the reaction of the photoproduct electrons with the organic molecule present into the solution and leads to its photoreduction. The constant rate is strongly dependent on the organic substance and, for the investigated molecules, passes from $1.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ for 4-fluorophenol to $7.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ for 4-bromophenol [11].

The second one, indicated as *pathway b*, illustrates the role of the oxygen. If the reaction occurs under aerobic conditions, the hydrated electrons could be captured by the dissolved oxygen, so forming the ion radical superoxide $\text{O}_2^{\cdot-}$ with a constant rate of $2.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ [5] (thus decreasing the available hydrated electrons). By adopting anaerobic conditions (cells filled with an inert gas) the oxygen competition can be strongly reduced, so favouring the occurrence of *pathway a*.

The third one describes the role of the solvent. The photogenerated electrons could react with the solvent (and H^+) with the formation of $\cdot\text{H}$ radical ($k = 2.1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$). Furthermore, this radical could react with the dissolved oxygen through the *pathway c* and lead to the formation of H_2O_2 (and finally $\cdot\text{OH}$ radicals), so inducing the formation of an oxidant species, or back react with $\cdot\text{H}$ radical ($k = 3.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) [24]. This last pathway could be depleted by adopting an anaerobic environment and appropriated pH conditions.

Likewise, the intermediate compounds formed during the halophenols degradation could be reduced themselves, so subtracting electrons and decreasing the process efficiency. The influence of the overall described competitive reactions



Scheme 1. Overall reactions involved in the electrons capture and transformation pathways followed by 2,4,5-trichlorophenol.

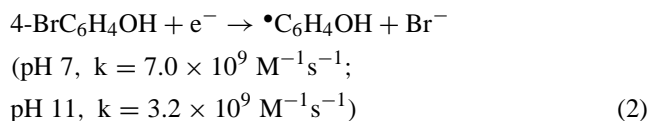
on the disappearance kinetic will be investigated for mono and polyhalophenols.

3.1. Monohalophenols

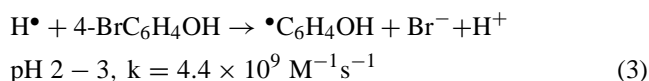
Table 1 reports the rates of disappearance for the investigated molecules. Looking closely to 4-bromophenol, the reaction mediated by hydrated electrons and the values quoted by pulse radiolysis may be described as shown below (reaction 2) [11]:

Table 1
Rate of disappearance of halophenols in presence of $\text{Fe}(\text{CN})_6^{4-}$ 1×10^{-3} M under anaerobic conditions

Halocompound	Rate, $\text{M} \times 10^{-7} \text{ s}^{-1}$
4-Brphenol pH 7	2.12
4-Brphenol pH 11	1.10
4-Fphenol pH 11	0.15
Phenol pH 7	0.10
2-Clphenol pH 7	0.63
4-Clphenol pH 7	0.67
2-Clphenol pH 11	0.45
3,4-Dichlorophenol pH 7	1.67
2,5-Dichlorophenol pH 7	1.63
2,4,5-Trichlorophenol pH 7	3.72



In addition, a competitive reaction with hydrogen radical could occur (reaction 3):



The profiles for disappearance and bromide evolution at pH 7 and 11 are displayed on Fig. 1 as a function of the irradiation time. In agreement with these rate constants assessed with pulse radiolysis, the rate of disappearance diminishes by increasing the pH (see Table 1 and Fig. 1); first-order decays are followed in both cases, with half life time passes from 7 to 13 min by varying the pH from 7 to 11. Contemporaneously to the 4-bromophenol disappearance, bromine is released as bromide ion. Closer inspection of the initial rate of bromide evolution reveals a ratio $v_{4\text{-BrC}_6\text{H}_4\text{OH}}:v_{\text{Br}^-} \sim 1$, so emphasizing the initial transformation pathway mainly occurs through a reductive dehalogenation.

The degradation of 2-chlorophenol at pH 7 and 11 is shown in Fig. 2. The reaction with hydrated electrons assessable with pulse radiolysis, together with the competitive

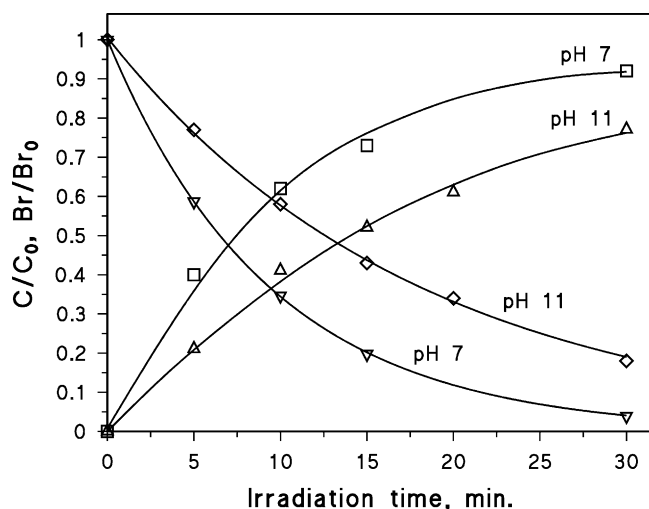
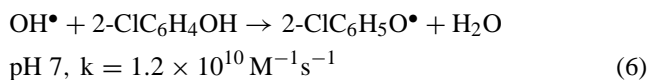
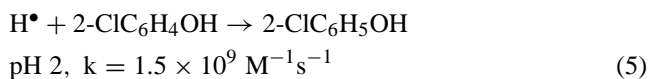
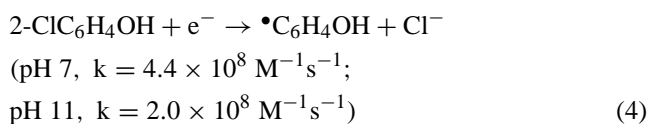


Fig. 1. Disappearance of 4-bromophenol (1.16×10^{-4} M) and bromide evolution under nitrogen with $\text{Fe}(\text{CN})_6^{4-} 1 \times 10^{-3}$ M at pH 7 and 11.

reactions mediated by the other radicals, are summarized on reactions 4–6.



The degradation rate for 2-chlorophenol slightly diminishes at increasing the pH, with $t_{1/2}$ passing from

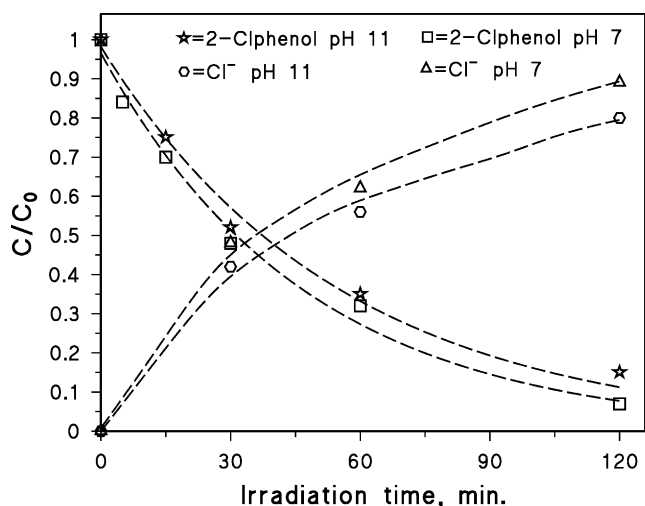


Fig. 2. Disappearance of 2-chlorophenol (1.56×10^{-4} M) and chloride evolution under nitrogen with $\text{Fe}(\text{CN})_6^{4-} 1 \times 10^{-3}$ M at pH 7 and 11.

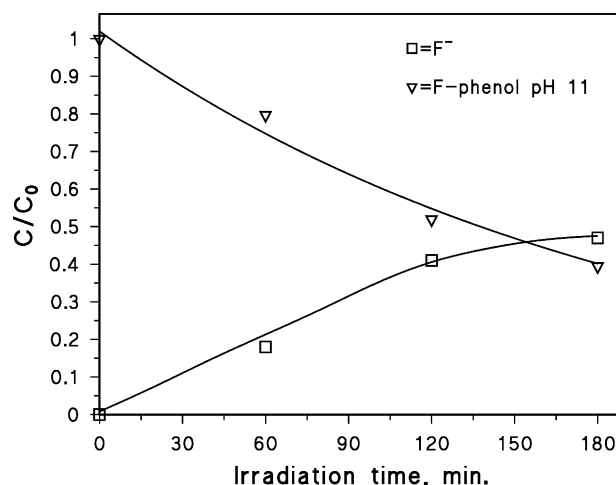
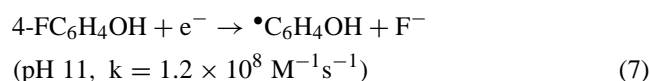


Fig. 3. Disappearance of 4-fluorophenol (1.79×10^{-4} M) and fluoride evolution under nitrogen with $\text{Fe}(\text{CN})_6^{4-} 1 \times 10^{-3}$ M at pH 11.

30 to 35 min; at pH 7 a rate of $6.3 \times 10^{-8} \text{ M sec}^{-1}$ has been observed. In parallel to the disappearance of the 2-chlorophenol, the chlorine atom is released as chloride ion at a rate comparable (the ratio $v_{2\text{-ClC}_6\text{H}_4\text{OH}}:v_{\text{Cl}^-}$ is ~ 1). The isomer 4-chlorophenol exhibits an analogous reactivity toward hydrated electrons and at pH 7 a rate of $6.7 \times 10^{-8} \text{ M sec}^{-1}$ has been quoted. Similarly, for 4-fluorophenol the reaction mediated by hydrated electrons can be described by reaction 7:



Also in this case, fluorine is released as fluoride ion with an evolution rate comparable with the rate of disappearance (Fig. 3).

The described results evidence that the rate of disappearance of the halophenols varies according to the type of the halogen atom; $v_{\text{Br-phenol}} > v_{\text{Cl-phenol}} > v_{\text{F-phenol}}$. Besides the dependence on the nature of the initial compound, a ratio between rate of disappearance and halide formation of 1:1 in all cases implies that monohalophenols have been mainly decomposed through a reductive dehalogenation pathway. It is also worth noting that the degradation process yields to formation of phenol as only intermediate from all the considered monohalophenols, so pointing out the occurrence of the reaction (8).



Phenol rate of reaction with hydrated electrons is considerable lower (see Table 1), so that its degradation is not observed in the investigated time.

According to the reactions 2, 4 and 7, the rate of disappearance of halocompounds can be described by the

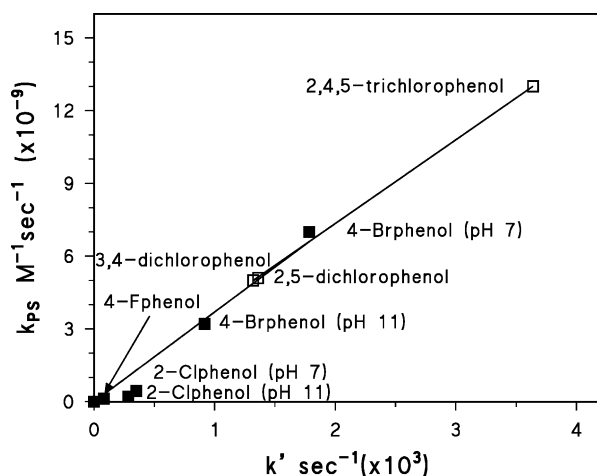


Fig. 4. Correlation between the rate obtained with $\text{Fe}(\text{CN})_6^{4-}$ and those estimated with pulse radiolysis. In empty square are reported the molecules investigated with ferrocyanide system for which do not exist a constant rate estimated with pulse radiolysis.

following equation:

$$V_{\text{Fe}(\text{CN})_6^{4-}} = k[e^-][\text{halophenol}] \quad (9)$$

The pseudo-first-order rate constants for halophenols disappearance ($k' = k[e^-]$) are plotted versus the pseudo-second-order rate constants obtained with pulse radiolysis (k_{PR}) in Fig. 4. Similarly to what observed in a previous work [9], a linear correlation between the value of rate constant calculated with the ferrocyanide system and the data estimated by pulse radiolysis exists.

Due to the good correlation between the rate constants estimated with the two techniques, it can be assumed that the pseudo-first-order constant obtained with $\text{Fe}(\text{CN})_6^{4-}$ corresponds to the second-order constant rate obtained with pulse radiolysis multiplied for the electron concentration. Thus, with this assumption the electron concentration in stationary state may be calculated as $[e^-] = k'/k_{\text{PR}}$, so that an average electron concentration of $2.4 \pm 0.3 \times 10^{-13} \text{ M}$ is obtained.

3.2. Polychlorophenols

A careful kinetic and mechanistic inspection has been carried out on dichlorophenols and 2,4,5-trichlorophenol. No literature data about the reaction rate with hydrated electrons are available for these molecules, so that it could be estimated by means of the correlation presented in Fig. 4.

The rate of disappearance of isomers 3,4- and 2,5-dichlorophenol has been investigated at pH 7, showing a pseudo-first-order constant rate of $1.35 \times 10^{-3} \text{ s}^{-1}$ and $1.30 \times 10^{-3} \text{ s}^{-1}$ for 3,4- and 2,5- dichlorophenol, respectively (see Table 1). By plotting these values in Fig. 4 (empty square) it can be approximate a reaction rate with hydrated electrons of $\sim 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value coincide with the one tabulated with pulse radiolysis for dichlorobenzenes [11]. A close similarity between the rate of reaction of halobenzenes and hydroxyhalobenzenes exists, so that

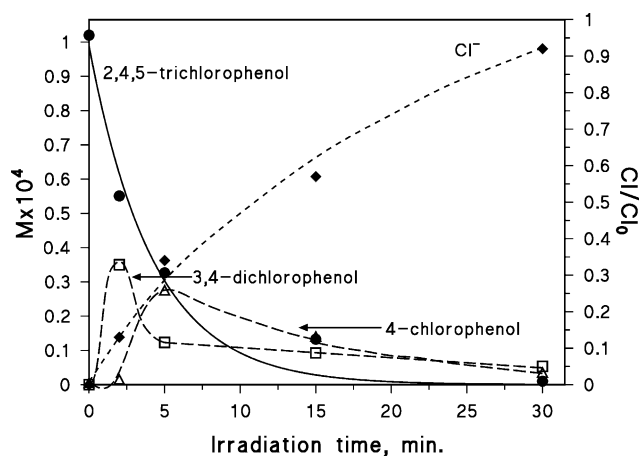


Fig. 5. Disappearance of 2,4,5-trichlorophenol ($1.02 \times 10^{-4} \text{ M}$), chloride evolution and intermediates formation under nitrogen with $\text{Fe}(\text{CN})_6^{4-}$ $1 \times 10^{-3} \text{ M}$ at pH 7.

the calculated value is in agreement with the expected reactivity toward electrons. Likewise, the two isomers exhibit similar reactivity toward hydrated electrons, so validating the behaviour previously observed with the chlorophenols.

2,4,5-Trichlorophenol degradation has been followed at pH 7 through the primary compound disappearance, the chloride formation and the intermediates evolution as evidenced in Fig. 5. A pseudo-first-order constant rate of $3.64 \times 10^{-3} \text{ s}^{-1}$ can be calculated (Table 1) so that, owing to the precedent discussed correlation, a second-order constant rate of reaction with electrons of $1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ can be estimated (Fig. 4, empty square).

Similarly to monohalophenols, the degradation occurs mainly through a reductive dehalogenation. As intermediate compounds, initially only 3,4-dichlorophenol has been observed; at 2 min of irradiation, when quite 50% of the 2,4,5-trichlorophenol is disappeared, it is accomplished by the formation of 3,4-dichlorophenol $3.7 \times 10^{-5} \text{ M}$. The high reactivity of TCP toward hydrated electrons directs toward a unique initial (reductive) pathway, so that on TCP initial degradation the competition of pathways *b* and *c* seems negligible.

Afterwards, 3,4-dichlorophenol is transformed into 4-chlorophenol (the maximum amount is reached at 10 min). After 30 min of irradiation, the complete disappearance of both the initial 2,4,5-trichlorophenol and the chlorinated intermediates is achieved. Simultaneously, formation of chloride ions in stoichiometric amount is a proof about a complete dechlorination and that no other chlorinated by-products are still present.

In an effort to clarify whether other minor pathways occur, we have examined in detail 3,4-dichlorophenol behaviour, being the main intermediate recognized from TCP disappearance. The temporal intermediates evolution is shown in Fig. 6. At 5 min of irradiation, quite 50% of the degraded 3,4-dichlorophenol is transformed into 4-chlorophenol through a reductive dehalogenation. A competitive oxidative

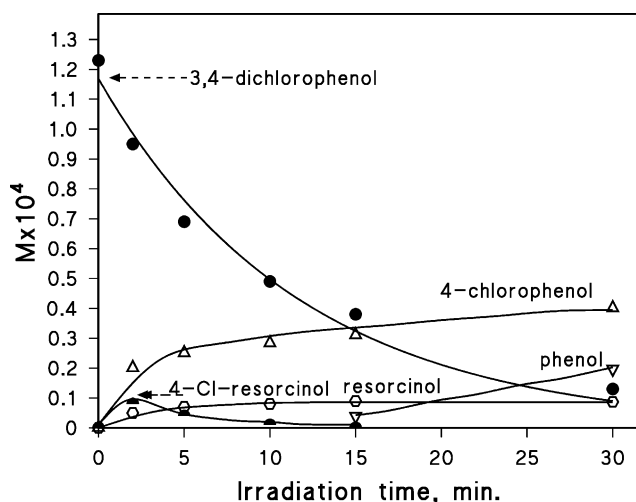


Fig. 6. Disappearance of 3,4-dichlorophenol (1.23×10^{-4} M) and intermediates formation under nitrogen with $\text{Fe}(\text{CN})_6^{4-}$ 1×10^{-3} M at pH 7.

reaction, probably mediated by $\bullet\text{OH}$ radicals, occurs and leads to the formation of small yield of 4-chlororesorcinol, so opening a secondary oxidative pathway. Indeed, the occurrence of an oxidative degradation seems linked to the persistence of oxygen in traces that, through the *pathway b* accomplishes to the formation of $\bullet\text{OH}$ radicals. These observations can be rationalized within the framework of the mechanism proposed in Scheme 1, which accounts for both the observed intermediates and the primary events occurring after ferrocyanide illumination. It can be seen that $\bullet\text{OH}$ radicals, formed from H_2O_2 dissociation, can back-react with $\bullet\text{H}$ or, alternatively, with organic molecules oxidizing them. Through this route, the hydroxychloroderivatives are probably formed.

For longer irradiation time phenol is formed through the reductive dehalogenation of 4-chlorophenol, while resorcinol is produced from the reductive dehalogenation of 4-chlororesorcinol. Both the hydroxylated benzenes react very slowly with hydrated electrons, so that in the investigated times they are resistant to a further degradation (see Fig. 6); no other benzenes intermediates have been identified.

Besides, similarly to what observed with heterogeneous photocatalysis treatment [25], the ferrocyanide system leads to the formation of condensation products. In particular, 4,4'-dichloro-3-hydroxybiphenyl and 4,4'-dichlorobiphenyl have been detected in traces. As arises from Scheme 1, an explanation may lie in the dimerization of 4-chlorophenol to 4,4'-dichlorobiphenyl, while 4-chlororesorcinol dimerization leads to 4,4'-dichloro-3-hydroxybiphenyl.

4. Conclusions

The reactivity of halophenols toward hydrated electrons obtained with ferrocyanide system shows a good correlation

with the data estimated by adopting pulse radiolysis, so emerging a further indication in favour to the employment of this method to assess the rate of reaction of organic compounds with hydrated electrons.

Additionally this method has been adopted to identify and quantify the by-products generated during the reductive process. Mono and polyhalophenols degraded mainly through a reductive dehalogenation process. In the present manuscript, we have focused on the case of polychlorophenols, for which a mechanism of transformation accounting for the recognized intermediates has been identified.

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