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Reactivity of chloromethanes with photogenerated hydrated electrons

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Abstract

Ferrocyanide ion illuminated with proper light has shown to generate hydrated electrons. The photogenerated solvated electron may interact with substances present in solution reducing organic compounds present in aqueous solution. We have investigated the reductive degradation of chloromethanes (tetrachloromethane, chloroform and dichloromethane) adopting ferrocyanide system under anaerobic conditions and the obtained results have been compared with those obtained with the pulse radiolysis; a good correlation between the rate of disappearance evaluated with the two techniques is achieved.

Keywords: Hydrated electrons; Photochemistry; Ferrocyanide; Chloromethanes

1. Introduction

The hydrated electron is a reactive species, highly reductive, that can be produced by the photolysis of the coloured dissolved organic matter (CDOM) in natural waters, of humic substances or other absorbing chromophores such as indoles and aromatic carboxylic acids [1–3]. The hydrated electron can influence the redox chemistry of natural waters both through the production of H_2O_2 and the reductive dehalogenation of organic pollutants in presence of CDOM [4].

We have evaluated the reactivity of several organic pollutants by adopting the ion ferrocyanide as source for hydrated electrons. The particular choice of the ferrocyanide ion under illumination is due to its efficient electron injection process that undergoes upon light-excitation [5]. When an aqueous solution containing $Fe(CN)_6{}^{4-}$ is irradiated with light at $\lambda < 350\,\text{nm}$, as following reaction takes place:

$$Fe(CN)_6{}^{4-} + h\nu \rightarrow Fe(CN)_6{}^{3-} + e^-_{aq} \qquad (1)$$

leading to the generation of hydrated electrons. Moreover, the ferrocyanide system has the advantage to form a single reactive radical (i.e. the hydrated electrons) [6].

The only additional primary process of the ferrocyanide system known to take place in parallel to the electron generation is the formation of the aquapentacyanoferrite complex [7]:

$$Fe(CN)_6{}^{4-} + H_2O \rightarrow Fe(CN)_5H_2O^{3-} + CN^- \qquad (2)$$

This system could be able to estimate the reaction rate of the organic compounds with the electrons. The photogenerated electrons, created through the reaction (1), can react with the dissolved oxygen to form the ion radical superoxide $O_2{}^{\bullet-}$ (thus decreasing the available hydrated electrons), or with an organic compound present into the solution. Adopting anaerobic conditions (cells filled with an inert gas) the oxygen competition can be eliminated.

In the present work, we have reported the rate of disappearance of molecules characterised by different reactivity toward the electrons. Their rates of disappearance will be compared with the rate constants obtained with pulse radiolysis, which is the method commonly adopted in estimating the reaction rate of the organic compounds with electrons.

2. Experimental

2.1. Material and reagents

Tetrachloromethane (Aldrich), trichloromethane (Aldrich), dichloromethane (Aldrich), and potassium ferrocyanide (Aldrich) were used as received. Sodium chloride (Merck), sodium fluoride (Merck) were used after drying.

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2.2. Irradiation procedures

Irradiation were carried out on 5 ml of solution containing 20 mg l^{-1} chloromethanes and $Fe(CN)_6^{4-}$ 1×10^{-3} 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 irradiation spectrum and the cells have been described elsewhere [8,9]. The total photonic flux (310–400 nm) in the cell and the temperature have been kept constant for all the experiments. They were 7.9×10^{-6} einstein min^{-1} and 50 °C, respectively.

Experiments were run at pH 7 and 11 after adjustment with NaOH. The experiments in absence of oxygen 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

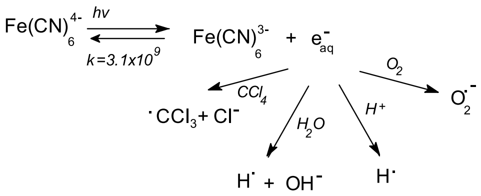
The contents of the cell were analysed by the appropriate analytical technique. The disappearance of the primary compound was followed using a purge and trap system (Tekmar LSC 2000) equipped with a Vocarb 3000 trap and a cryofocusing module connected with a 60 m DB5 column (Supelco, 0.32 mm i.d., 0.25 μm coating). The purge and trap's and GC operative parameters have already been reported. GC Varian STAR 3400 with a FID detector was utilised. Under the reported condition [9], the retention times were 4.45, 5.26, 6.03 min for CH_2Cl_2, $CHCl_3$ and CCl_4 respectively.

A Dionex DX 500 apparatus equipped with a ED40 electrochemical detector and a GP40 gradient pump was used for the chloride analysis. By utilising an AS9HC anionic column and an alkaline buffer eluant containing $NaHCO_3$ (5 mM) and Na_2CO_3 (12 mM) at the flow rate of 1 ml min^{-1}, the retention time of chloride was 5.5 min.

3. Results and discussion

Differently from pulse radiolysis, where the primary event is followed (i.e. $CCl_4 + e^- \rightarrow {}^{\bullet}CCl_3 + Cl^-$), in stationary state the electrons formed through reaction (1) can react with the initial compound (i.e. CCl_4), but while proceeding the reaction they can also react with both the generated intermediates and the $Fe(CN)_6^{3-}$ itself ($k = 3.1 \times 10^9\ M^{-1}\ s^{-1}$).

The main competitive reactions involved in the ferrocyanide system, when an organic compound is present (i.e. CCl_4), are summarised in Scheme 1. These reactions can be subdivided as follows.



Scheme 1. Overall reactions involved in the ferrocyanide system.

(a) Reactions of the photogenerated electrons with oxygen and H^+ [10]

$$e^- + O_2 \rightarrow O_2^{\bullet -} \qquad k = 2.0 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (3)$$

$$e^- + H^+ \rightarrow H^{\bullet} \qquad k = 2.2 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (4)$$

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \qquad k = 2.1 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (5)$$

The oxygen competition could be neglected by working under anaerobic conditions, so that the available electrons are increased. The experiments described below have been performed under nitrogen, so that the competition of the reactions (3) and (5) can be considered negligible.

(b) Reactions of the photogenerated electrons with the chloromethanes:

$$e^- + CCl_4 \rightarrow {}^{\bullet}CCl_3 + Cl^- \qquad (pH\ 7)\ k = 1.6 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (6)$$

$$e^- + CHCl_3 \rightarrow {}^{\bullet}CHCl_2 + Cl^- \qquad (pH\ 7)\ k = 3.0 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (7)$$

$$e^- + CH_2Cl_2 \rightarrow {}^{\bullet}CH_2Cl + Cl^- \qquad (pH\ 10)\ k = 6.3 \times 10^{9}\ M^{-1}\ s^{-1} \qquad (8)$$

(c) Reactions of the chlorocompounds with hydrogen radical, generated through the reaction (4):

$$H^{\bullet} + CCl_4 \rightarrow {}^{\bullet}CCl_3 + Cl^- + H^+ \qquad k = 3.8 \times 10^{7}\ M^{-1}\ s^{-1} \qquad (9)$$

$$H^{\bullet} + CHCl_3 \rightarrow {}^{\bullet}CHCl_2 + {}^{\bullet}CCl_3 + HCl + H_2 \qquad k = 1.1 \times 10^{7}\ M^{-1}\ s^{-1} \qquad (10)$$

$$H^{\bullet} + CH_2Cl_2 \rightarrow {}^{\bullet}CHCl_2 + {}^{\bullet}CH_2Cl + HCl + H_2 \qquad k = 4.0 \times 10^{6}\ M^{-1}\ s^{-1} \qquad (11)$$

In the presently investigated pH conditions the reactions (9)–(11) can be disregarded (being of 3 orders magnitude lower than the other competitive reactions), while the role played by the remaining reactions has been evaluated on the chloromethanes photoreduction and it will be discussed below.

3.1. Tetrachloromethane photoreduction

The disappearance of the CCl_4 at pH 7 under nitrogen, together with the evolution of chloride, is shown in Fig. 1. CCl_4 is quickly photoreduced ($t_{1/2} = 5$ min), according to

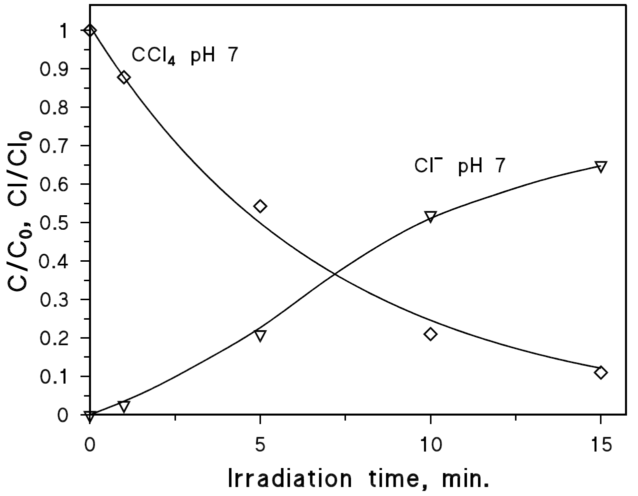


Fig. 1. Disappearance of CCl_4 (1.3×10^{-4} M) and chloride evolution under nitrogen with $Fe(CN)_6{}^{4-}$ 1×10^{-3} M.

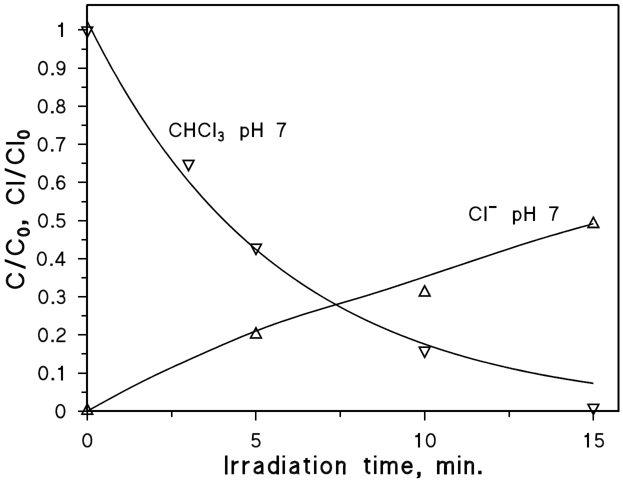
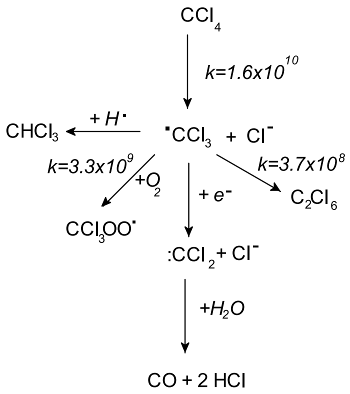


Fig. 2. Disappearance of $CHCl_3$ (1.7×10^{-4} M) and chloride evolution under nitrogen with $Fe(CN)_6{}^{4-}$ 1×10^{-3} M.

reaction (6). A comparison between the kinetic evolution of chloride and the rate of disappearance of tetrachloromethane can be useful in distinguishing the role played by the different species involved in the process. It can be possible to discriminate between the initial rate, due to the reaction of CCl_4 with hydrated electrons (reaction (6)) and the successive degradation, where the competition of other organic compounds could be important. In presence of illuminated ferrocyanide system the CCl_4 molecule could undergo several competitive reactions, as summarised on Scheme 2. In previous works, adopting titanium dioxide as photocatalyst [11–13], chloroform and dichloromethane have been found as intermediates from the degradation of CCl_4. These species could be similarly formed also in the present experimental conditions, so competing with the CCl_4 for the electrons capture.

Looking closely to the initial rate of chloride evolution, by considering that four chlorine atoms are contained in the initial compound, the ratio $v_{CCl_4} : v_{Cl^-}$ is ~1:1 only in the initial period of irradiation, where the rate of disappearance is only due to the direct reaction of CCl_4 with electrons. Further degradation follows a ratio $v_{CCl_4} : v_{Cl^-} = 1 : 2$, so suggesting that the competition between the reactions (6) and the formation of species through the loss of two Cl atoms occurs (i.e. the formation of $:CCl_2$ radical and the further conversion to CO, see Scheme 2). Finally, at 15 min when 90% of the initial compound has been degradated, the ratio $v_{CCl_4} : v_{Cl^-}$ becomes 1:3, so stressing the competition between reaction (6) and the intermediates reactions is markedly increased.



Scheme 2. Overall reactions that could be involved in the tetrachloromethane degradation.

3.2. Trichloromethane photoreduction

Chloroform, whose profile of disappearance and chloride formation are reported in Fig. 2, rapidly reacts with the photogenerated electrons ($t_{1/2} = 4$ min). Until 10 min of irradiation, when 85% of the initial compound is disappeared, the ratio between the $CHCl_3$ disappearance and the chloride evolution (rate multiplied for the number of chlorine contained in the chloromethane) still remains $v_{CHCl_3} : v_{Cl^-} = 1 : 1$. In this range of time, the reaction of chloroform with the hydrated electron photogenerated is the only one occurring in an appreciable amount. The role of reaction (8) is no more negligible for longer irradiation time, being the ratio between $CHCl_3$ and Cl^- slightly increased ($v_{CHCl_3} : v_{Cl^-} = 1 : 1.5$). Similarly to what observed with CCl_4, also in this case, the chlorine could be simultaneously released from $CHCl_3$ and from intermediates (through the loss of 2 Cl atoms, i.e. by means of the formation of $:CCl_2$ radical).

3.3. Dichloromethane photoreduction

In Fig. 3 the disappearance of CH_2Cl_2 ($t_{1/2} = 10$ min) can be observed. The rate of disappearance of CH_2Cl_2 looks closely the rate of chloride evolution (ratio $v_{CH_2Cl_2} : v_{Cl^-} = 1 : 1$). This implies that the reaction of dichloromethane with electrons (reaction (8)) could be in competition only

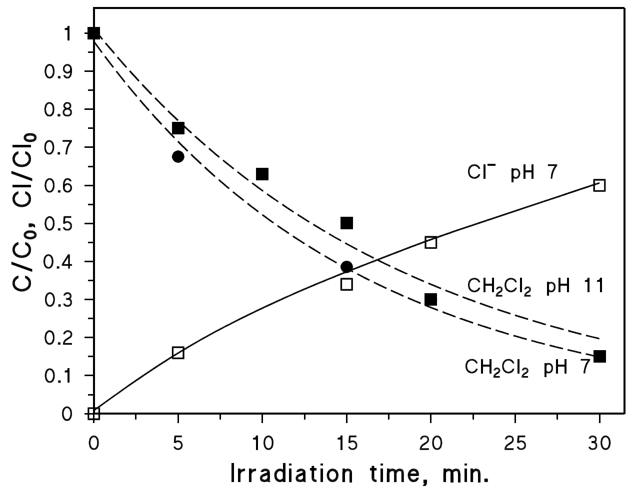


Fig. 3. Disappearance of CH_2Cl_2 (2.4×10^{-4} M) and chloride evolution under nitrogen with $Fe(CN)_6{}^{4-}$ 1×10^{-3} M.

with the formation of intermediates formed consequently to the release of a chlorine atom (i.e. CH_3Cl).

Being this chlorocompound negligibly influenced by other competitive reactions and the one presenting the lower reaction rate, it could be adopted to evaluate the role of H^+. The reaction (4) becomes significant only at very acidic conditions, but unfortunately at pH < 5 the ferrocyanide anion is no more photochemically stable; a colour-changing of the irradiated solution occurs, so indicating that the species involved in the photochemical process are no more the same. Being available the constant rate of pulse radiolysis at pH 10 [10], thus we have investigate if in basic conditions the mechanism of reaction still remains the same. By comparing the rate of disappearance of dichloromethane at pH 7 and 11 (see Fig. 3 and Table 1), the calculated rate passes from $2.47 \times 10^{-7}\,\mathrm{M\,s^{-1}}$ (pH 7) to $2.15 \times 10^{-7}\,\mathrm{M\,s^{-1}}$ (pH 11), so that the variations can be considered negligible (in the pH range 7–11).

3.4. Correlation among the different constant rates

According to the reactions (6)–(8), the rate of disappearance for the investigated chlorocompounds can be valued through the following equation:

$$v_{Fe(CN)_6{}^{4-}} = k[e^-][\text{chloro compound}] \qquad (12)$$

Table 1
Rate of disappearance of chloromethanes under nitrogen with $Fe(CN)_6{}^{4-}$ 1×10^{-3} M

Chlorocompound	Rate ($\times 10^7\,\mathrm{M\,s^{-1}}$)
CH_2Cl_2, pH 7	2.47
CH_2Cl_2, pH 11	2.15
$CHCl_3$, pH 7	4.93
CCl_4, pH 7	3.07

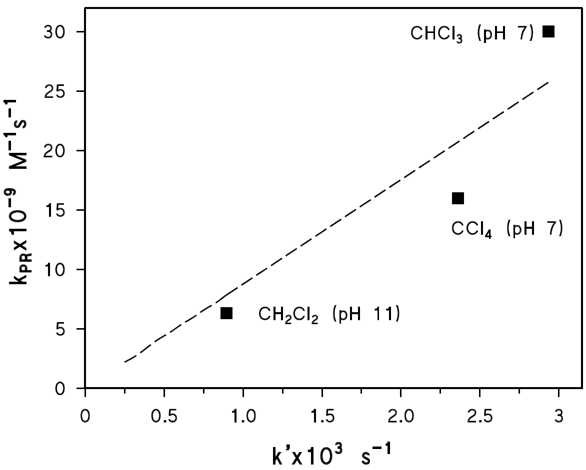


Fig. 4. Correlation between the constant rate obtained with $Fe(CN)_6{}^{4-}$ (k') and those estimated with pulse radiolysis (k_{PR}).

In Fig. 4 is shown the pseudo-first-order rate constant of disappearance of the chlorocompounds (k') plotted versus the second order rate constants obtained with pulse radiolysis (k_{PR}). The value of rate constant calculated with the ferrocyanide system shows a quasi-linear correlation with the data estimated by adopting pulse radiolysis, so emerging a first indication in favour to the employment of this method to assess the rate of reaction of chloromethanes with hydrated electrons. Differently from pulse radiolysis, competitive reactions may occur, so bringing to deviation from the linearity.

By existing a good correlation between the rate constants estimated with the two techniques, it can be assumed that the pseudo-first-order constant obtained with $Fe(CN)_6{}^{4-}$ coincides with 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 $[e^-] = k'/k_{PR}$, so that an average electron concentration of $1.2 \times 10^{-13} \pm 0.3$ M is obtained.

It can also be estimated the photonic efficiency of the process, calculated as the ratio between the rate of disappearance of the organic compound and the flux incoming into the cell [14,15]. The photonic efficiency calculated for this chlorocompounds ranges from 0.94% for CH_2Cl_2 transformation to 1.87% for $CHCl_3$.

4. Conclusions

The reactivity of chloromethanes toward hydrated electrons obtained with ferrocyanide system show a good correlation with the data estimated by adopting pulse radiolysis, so that this method could represent an alternative to the pulse radiolysis in evaluating the reactivity of organic compounds toward hydrated electrons. Moreover, this method could be used to estimate not only the electrons rate of reaction, but also in identifying and quantifying the by-products generated during the process. In the studies performed with pulse radiolysis, few investigations on the reaction products are available, so that the ferrocyanide system could be adopted as a complementary technique by representing a good tool for investigations on the reaction mechanism in steady-state conditions.

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