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## Radiation induced dechlorination of some chlorinated hydrocarbons in aqueous suspensions of various solid particles

V. Múčka<sup>a,\*</sup>, M. Buňata<sup>a</sup>, V. Čuba<sup>a</sup>, R. Silber<sup>a</sup>, L. Juha<sup>b</sup><sup>a</sup> Czech Technical University, Faculty of Nuclear Sciences and Physical Engineering, 115 19 Prague 1, Czech Republic<sup>b</sup> Institute of Physics AS CR, v.v.i., Department of Radiation and Chemical Physics, 182 21 Prague 8, Czech Republic

## H I G H L I G H T S

- The active carbon affects negatively the dechlorination of aliphatic hydrocarbons.
- The inhibition effect is connected with the adsorption of hydrocarbons.
- The CuO oxide inhibits the mineralization of the perchloroethylene.
- None of the two modifiers changes the reaction order of radiation induced dechlorination.

## A R T I C L E I N F O

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## A B S T R A C T

Radiation induced dechlorination of trichloroethylene (TCE) and tetrachloroethylene (PCE) in aqueous solutions containing the active carbon (AC) or cupric oxide (CuO) as the modifiers was studied. The obtained results were compared to the previously studied dechlorination of polychlorinated biphenyls (PCBs). Both modifiers were found to decrease the efficiency of dechlorination. The AC modifier acts mainly *via* adsorption of the aliphatic (unlike the aromatic) hydrocarbons and the CuO oxide mainly inhibits the mineralization of the perchloroethylene. The results presented in this paper will be also helpful for the studies of the impact of chlorinated hydrocarbons on the membrane permeability of living cells.

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## 1. Introduction

Halogeno-organic compounds (including polychlorinated biphenyls – PCBs) are dangerous and hazardous compounds. In fact, the halogenated organic compounds may cause disorders in a cell-division leading to the cancer development. They may also modify the function of impregnating substances in the cell walls, such as lipids or phospholipids (Omann and Lakowicz, 1982; Bach and Sela, 1984; Suwalsky et al., 1997a,b), and thus affect their permeability. (Similarly, the gamma or EB irradiations may damage the cell membrane of living cells (Shim et al., 2012; Nayefi et al., 2014)). Therefore, the disposal of the halogenated hydrocarbons

became an urgent task since the turn of the 20th and 21st centuries (Getoff, 1996). The persistent chlorinated organic pollutants such as PCBs or organochlorine pesticides may emerge also nowadays even in quite pristine environments such as the Southern Ocean region (Galbán-Malagón et al., 2013) or in continental shelf sediments of the Western Antarctic Peninsula (Zhang et al., 2013). It is obvious that the destruction of pollutants in these natural materials using expensive conventional incineration (> 1100 °C) methods is quite unthinkable in practice. Environment-friendly methods are necessary also for detoxification of the cells in living organisms. That is a reason why alternative effective methods are needed. One of them is, in general, the radiation treatment of the polluted substances or the catalytic decomposition of chlorinated pollutants (Múčka et al., 2004) or the hybrid radiation-catalytic methods (Son et al., 2010) in which a synergetic effect may occur (Shaoqing et al., 2010). Above all, a

\* Corresponding author. Fax: +420 224 358 202

E-mail address: [viliam.mucka@jfifi.cvut.cz](mailto:viliam.mucka@jfifi.cvut.cz) (V. Múčka).

suitable hybrid method may be considered to be convenient also for application in the presence of living organisms. A special combined method is the radiation treatment in the presence of various modifiers. Searching for some convenient modifiers is, therefore, the most actual task (Múčka et al., 2000a). It was already earlier found out that the oxygen promotes radiation induced degradation of some chlorinated hydrocarbons (Getoff and Lutz, 1985; Homlok et al., 2012; Zona et al., 2012) including pesticides (Dessouki et al., 1999). Significantly higher positive effect was observed when the combination of ionizing radiation treatment with ozonation was used in the decomposition of the pentachlorophenol (He et al., 1997), trichloroethylene (TCE), tetrachloroethylene (perchloroethylene, PCE) (Gehring et al., 1995; Múčka et al., 2003a) or 2-chloroaniline (Winarno and Getoff, 2002). A positive effect of the nitrous oxide was also observed (Múčka et al., 2003b, 2009) but not as high as in the case of ozone (Gehring and Eschweiler, 2002). A relatively high attention has been devoted to the impact of hydrocarbonate or nitrate ions. The last mentioned ions evidently change the mechanism of dechlorination of 2,4-dichlorophenol and thus decrease the efficiency of radiation dechlorination (Drzewicz et al., 1999). Somewhat different situation was found in the case of hydrocarbonate ions. Although a negative effect was observed in the dechlorination of both perchloroethylene (Múčka et al., 2003b,c) and 2,4-dichlorophenol (Drzewicz et al., 1999), no impact was found in dechlorination of p-chlorophenol (Bettoli et al., 1998) and a positive influence was detected in the case of chloroform dechlorination (Múčka et al., 2003c). The explanation of such rather diverse results was proposed in the earlier cited paper (Múčka et al., 2004). A great positive effect of hydrogen peroxide with a synergic feature was proven in the radiation degradation of chlorophenols which resulted in an increased efficiency of dechlorination and a TOC (total organic carbon) removal. Both these parameters were found to be proportional to the absorbed dose (Hu and Wang, 2007). A positive influence of some surfactants (e. g. RA-40™) on the radiation degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) led to a high conversion (90–98%) in a contaminated soil (Hilarides et al., 1994; Gray and Hilarides, 1995). Ionizing radiation was effective in degradation of PCBs in micellar solutions but scavenging of hydrated electrons by surfactant led to the decrease in reaction efficiency (Schmelling et al., 1998). A special attention has been devoted to solid modifiers, namely to the TiO<sub>2</sub> oxide. However, the obtained results are rather diverse (González-Juárez and Jiménez-Becerril, 2006; Yang et al., 2007; Múčka et al., 2000a; Getoff, 2002; Jung et al., 2002). A positive influence of other oxides such as aluminium oxide or silicon oxide on radiation induced dechlorination of 4-chlorophenol was explained (González-Juárez and Jiménez-Becerril, 2006) by a transformation of the surface hydroxyl groups to the OH· radicals. The ZrO<sub>2</sub> catalyst enhanced the radiation degradation of 4-chlorophenol and simultaneously decreased its toxicity in a complex effluent matrix (Kang et al., 2011). It would be interesting to find out whether the above mentioned findings are valid also for other types of chlorophenol molecules, since it was found (Peng et al., 2012) that the number and position of chlorine atoms in the benzene ring has a significant influence on the dechlorination of chlorophenols. A significant positive effect of cuprous oxide (Cu<sub>2</sub>O) was observed in radiolytic dechlorination of PCBs (DELOR 103 and DELOR 106) when the suspension in alkaline 2-propanol solution was treated by the EB radiation (Múčka et al., 2000a, 2002). In this reaction, a large negative impact was described in the presence of both PbO and NiO and partially also in the presence of zeolite catalyst (Múčka et al., 2000a). The dechlorination of PCBs may be also affected by the active carbon as a promoter of the radiation induced process (Múčka et al., 2000a, 2002). With dehalogenation of trichlorotrifluoroethane (CFC-13) on the surface of molecular sieve

13X irradiated with gamma rays in a 2-propanol solution, the adsorption of halogenated substrate may be an important process (Yamamoto and Tagawa, 1998).

The aim of this paper is to examine the impact of two solid modifiers especially active carbon (AC) and cupric oxide (CuO) on the dechlorination of TCE and PCE hydrocarbons. The obtained results will be compared with those published earlier for dechlorination of PCBs (DELOR 103 and DELOR 106) in presence of the same modifiers. A special attention will be devoted to the order of dechlorination of PCBs with regard to the order of radiation induced dechlorination of aliphatic hydrocarbons studied earlier (Múčka et al., 2009). The obtained knowledges may be useful for the solution to the influence of chlorinated hydrocarbons on permeability of cell membranes because the molecular mechanisms of chlorinated hydrocarbons action are poorly understood and the exact mechanism of the action is not well known. It is clear that they act at the cell membrane level. The lipophilicity of most chlorinated hydrocarbons such various pesticides makes lipid- or phospholipid-rich membranes a possible target of their interaction with living cells. It seems to be true that the toxicity of chlorinated hydrocarbons may be due to the changes in membrane fluidity (Suwalsky et al., 1996, 1997a,b).

## 2. Experimental

All used chemicals were of analytical grade purity. Aqueous solutions of TCE and PCE with concentrations ranging from  $1.6 \times 10^{-4}$  to  $405 \times 10^{-4}$  vol% and from  $2.7 \times 10^{-4}$  to  $94 \times 10^{-4}$  vol%, respectively, were irradiated with accelerated electrons ( $E=4.5$  MeV, dose rate  $D^* 1.5$  kGy s<sup>-1</sup> and absorbed doses  $D$  from 0.5 to 5.0 kGy) in sealed glass ampoules. Prior to irradiation, different amounts of modifiers, i. e. active carbon (AC) or cupric oxide (CuO), were added to the solutions of chlorinated hydrocarbons so that their concentrations ranged from 0.1 to 5.0 g dm<sup>-3</sup>. A mean size of solid particles of active carbon was from 0.6 to 3 mm and their specific surface area was 380 m<sup>2</sup> g<sup>-1</sup>. The CuO oxide was heat treated at 300 °C for 5 h prior its use. The grain size was 0.1 mm and the mean specific surface area of about 15 m<sup>2</sup> g<sup>-1</sup>. The whole system was agitated in the course of irradiation so that the modifier particles were dispersed in the solution. The concentrations of hydrocarbons (determined by means of a gas chromatography) and the chloride ions (determined electrochemically) were determined with the total average relative error of  $\pm 15$  and  $\pm 21\%$ , respectively. The data on the concentration of the Cl<sup>-</sup> ions after the irradiation ( $c_{\text{Cl}^-}$ ) were reduced by the data prior to irradiation ( $c_{\text{Cl}^-}^0$ ). More details on chemical analysis, technique and dosimetry as well as on the dechlorination of the PCE and the PCBs both in alkaline 2-propanol solution are available in earlier articles (Múčka et al., 1977, 1999, 2003a,b,c, 2004). Following quantities have been calculated:

- The degrees of dechlorination  $\alpha$  (CHC) [%] =  $100 (c_{\text{CHC}}^0 - c_{\text{CHC}}) / c_{\text{CHC}}^0$  (degradation) or  $\alpha$  (Cl<sup>-</sup>) [%] =  $100 (c_{\text{Cl}^-} - c_{\text{Cl}^-}^0) / nc_{\text{CHC}}^0$  (mineralization), where  $\alpha$  (CHC) and  $\alpha$  (Cl<sup>-</sup>) are the degrees of dechlorination determined from the decreasing concentration of chlorinated hydrocarbons (CHC) and from the increasing concentration of the chloride ions (Cl<sup>-</sup>), respectively,  $c_{\text{CHC}}^0$  and  $c_{\text{Cl}^-}^0$  are the concentrations of chlorinated hydrocarbons and chloride ions prior to the irradiation, respectively and  $c_{\text{CHC}}$  and  $c_{\text{Cl}^-}$  represent the above mentioned quantities after the irradiation. The symbol  $n$  determines the number of chlorine atoms in one molecule of chlorinated hydrocarbon.
- The relative radiation chemical yields  $G$  (-CHC) [ $10^{-2}$  eV<sup>-1</sup>] or  $G$  (Cl<sup>-</sup>) [ $10^{-2}$  eV<sup>-1</sup>] (generally  $G$ ) are defined as  $G = 100c_{\text{N}_2e}/\rho D$  where  $c$  is the change in the concentration of the hydrocarbon

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