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Oxidative Degradation of 2,4,6-Trichlorophenol in the Presence of Air Ions

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Abstract: 2,4,6-trichlorophenol (TCP) was firstly treated with air ions generated by electric discharge, and high dechlorination (53%) was observed after 60 min treatment, indicating that air ions are an efficient dechlorination means and might have a future in the oxidative removal of chlorinated phenols. In addition, a stepwise degradation of TCP, beginning with the formation of a major product 2,6-dichloro-1,4-benzenediol *via* substitution, is proposed through a detailed analysis of gas chromatography/mass spectrometry.

Keywords: 2,4,6-Trichlorophenol, air ions, electric discharge, oxidative degradation, pollutant treatment.

As a result of its widespread use in industry and agriculture[1], 2,4,6-trichlorophenol (TCP) becomes one of the most important pollutants in the environment (aqueous systems and soils). Furthermore, TCP is persistent, and polychlorinated dibenzo-p-dioxins and dibenzo-furans have also been found in chlorophenol-contaminated soils[2]. Therefore, the removal of TCP from the environment has invoked a great attention[3], and various treatment techniques have been proposed for this purpose, involving catalytically oxidative degradation with different catalysts[4,5]; chemical decomposition of TCP by ozone, Fenton’s reagent and UV radiation[6]; detoxification by ionizing radiation (γ-ray)[7] and reductive dechlorination by anaerobic-aerobic technique[8]. However, only the treatment techniques which are simple, inexpensive and can achieve complete mineralization, are favorable.

Air ions especially negative air ions generated by electric discharge have been widely used for food preservation[9,10], and today are known as an important technique for pollutant treatment[11,12], due to their environmentally friendly behavior. Namely, these air ions are generally composed of $H^+(H_2O)_n$, $CO_3^-(H_2O)_n$, $O_2^-(H_2O)_n$, $NO_2^-(H_2O)_n$, NO_3^-, O^- and O_3^-[13]; they are rather active, and apt not only to react with organic pollutants to cause degradation, but themselves also to decompose to form environmentally compatible products. Hence, air ions are an attractive tool for waste removal. However, little is known on their potential use in degrading TCP, a major and recalcitrant pollutant produced by paper mills. This prompted us to make such an attempt, and herein we report the primary results of degrading TCP with air ions generated by electric discharge.

Experimental

The generator for air ions by electric discharge and the treatment setup were used as described previously[12]. A 500 mL solution containing the desired concentration (typically 2 mM) of TCP was prepared in water, and transferred into the treating cell. The compressed air containing air ions with a flow rate of 0.014 m^3/min was then bubbled through the solution at 23±2 °C. Here the solutions were treated for periods of 20 min and 60 min, respectively, to obtain different degradation products. The concentrations of the released Cl^- ions in the treated solution were determined by ion chromatography.

A 40 mL portion of the treated solution was then evaporated to dryness in a rotary evaporator under reduced pressure. The residue was dissolved in 0.5 mL acetone, applied to thin layer plates, and separated primarily with acetone/n-hexane (5:2). The detection of zones was based on the human eye aided sometimes by iodine vapor or UV light. Major zones, depending on their area and intensity, were recovered by scraping them off, extracting the substance with acetone, and separating the residual adsorbent with syringe filters (1.0 μm, PTFE). The obtained acetone filtrates were dried with N_2, and the residues were then analyzed by means of ^1H NMR or GC-MS. In this way, 5 zones were visualized for the treated solution of 20 min, and two main zones A and B with $R_f = 0.24$ and $R_f = 0.89$ were collected, respectively. Similarly, for the treated solution of 60 min, 8 zones can be detected and one main zone C with $R_f = 0.91$ was collected. In the meantime, a blank sample was treated under the same conditions for comparison purpose.

Results and Discussion

The addition of $AgNO_3$ to the untreated TCP solution did not produce any precipitate, whereas the Cl^- ions released in the TCP treatment were confirmed by the formation of AgCl white precipitate. It was found that the numbers of Cl^- released in the treated solutions of 20 min and 60 min were 0.6 Cl^- ions and 1.6 Cl^- ions per TCP molecule, and thus the corresponding dechlorination ratios of TCP are 20% and 53% (**Table 1**), respectively. Under the present conditions, a longer treating time such as 2 h did not considerably improve the dechlorination ratio, but the pH of the solution decreased from 5 at the beginning to 2.5 (**Table 1**), indicating that further degradation occurred and the degradation products might contain more acidic groups like carboxyl. The Cl^- release data suggest that air ions are a simple and efficient dechlorination means although a small amount of TCP substrate possibly remains in the solution.

Table 1 The Cl^- release in the TCP (2 mM) treatment with air ions generated by electric discharge

Treating time (min)	pH	Cl^- concentration (mM) [a]	Number of Cl^- released per TCP	Dechlorination ratio (%, molar basis)
20	4	1.21± 0.02	0.6	20
60	3	3.19± 0.01	1.6	53
120	2.5	3.53± 0.01	1.8	58

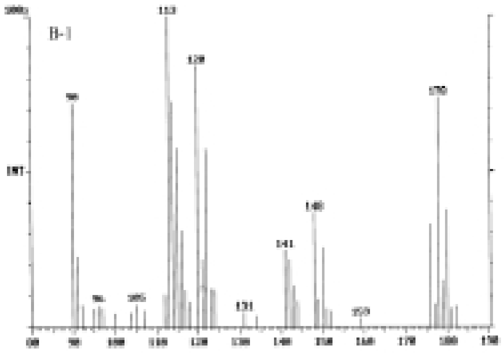
[a] Results of two determinations.

The above residues obtained from the zones A, B, C and the blank were dissolved in CD_3COCD_3 and subjected to ^1H NMR and GC-MS analyses. Under the given conditions, the blank yielded an unidentified peak with a retention time of 12:15 (min:sec), which appeared in all cases of A, B and C, while TCP has a retention time of 13:45.

The main component in the zone A was the remaining and unchanged TCP, since it gave the same retention time (13:45) and mass spectra as TCP itself, suggesting that 20 min of treating time is not enough to cause a full conversion of the substrate TCP (2 mM).

Zone B contained four components B-1, B-2, B-3 and B-4, whose retention times were 11:40, 14:04, 16:48 and 17:53, respectively. **Figure 1** shows the mass spectra of B-1. On the basis of fragments, and a molecular ion peak cluster typical for a molecule having two Cl atoms {182[$(M+4)^+$, 6.5(relative intensity)], 180[$(M+2)^+$, 38], 178(M^+, 73), 176[$(M-2H)^+$, 32], 148[$(M-2H-CO)^+$, 36], 141[$(M-2H-Cl)^+$, 24], 120(82), 113(100)}, B-1 was identified as 2,6-dichloro-1,4-benzenediol. Similarly, B-2 was assigned as 3,5-dichlorocatechol, but its two hydrogen atoms in hydroxyl groups were deuterated since the sample residue was dissolved in CD_3COCD_3. B-3, an isomer of B-2, was the deuterated B-1, *i.e.*, 2,6-dichloro-1,4-benzenediol but with two hydrogen atoms deuterated in hydroxyl groups. This component was the major product in zone B according to its largest peak in the GC measurements, suggesting that under the present conditions the oxidative dechlorination of TCP to form 2,6-dichloro-1,4-benzenediol is the first step and a main pathway. This indicates again that the Cl atom at para-position tends to be replaced easily by –OH group[14].

Figure 1 Mass spectra (EI) of B-1



Because acetone was employed as solvent for the TCP standard solution, its presence in the treated solution may lead to the formation of other coupling side-products, and B-4 may be such a kind of product. According to its mass spectra typical for a compound containing two chlorine atoms {225[$(M+4)^+$, 2.9], 223[$(M+2)^+$, 19.7], 222[$(M+H)^+$, 42.3], 221(M^+, 30.7), 206[$(M-CH_3)^+$, 100], 178[$(M-CH_3-CO)^+$, 5.8], 149[$(M-CH_3-CO-HCO)^+$, 11.4], 141(46.4)}, B-4 was tentatively assigned as 2,6-dichloro-4-acetoxyphenol whose hydrogen atom in the hydroxyl group was also deuterated. ^1H NMR analysis gave a very limited information due to the components in the zone B being a mixture, but the resonance signal occurring at the region of δ 2.0-2.3 ppm may be attributed to the presence of methyl groups. In addition, the ^1H NMR spectra showed no resonance signal at lower field ($\delta > 9$ ppm), also supporting that the substitution of the chlorine atom by hydroxyl group mainly occurs at the para-position. Otherwise the signal of a proton should appear at the lower field, if the ortho substitution took place and therefore 2,4-dichloro-6-acetoxyphenol should be produced in moderate quantities accompanying the formation of an intramolecular hydrogen bond.

The light yellow zone C, obtained after the 60 min treatment of TCP, showed two components (C-1 and C-2) with the retention times of 16:48 and 17:53, respectively, identical to those of B-3 and B-4 in the zone B. Furthermore, their mass spectra were identical to those of B-3 and B-4, respectively. Therefore, C-1 and B-3 are the same component, and so is the other pair (C-2 and B-4). It should be mentioned that the component B-2 disappeared completely in the zone C, indicating that B-2 is unstable and more degradable, consistent with the literature report that an aromatic ring having two ortho hydroxyl groups is readily cleaved[15]. Also, the largest peak in the GC traces is C-1, whose precursor 2,6-dichloro-1,4-benzenediol is thus the major product in the zone C.

In conclusion, the oxidative degradation of TCP has been firstly studied with air ions generated by electric discharge. The initial step is to yield the major product 2,6-dichloro-1,4-benzenediol as well as a minor one 3,5-dichlorocatechol by substitution of the nucleophiles (OH^-, O^-, etc) attacking on the aromatic ring. Of course, other minor compounds and even further degradation products are not included owing to their smaller quantities or not identifying them. In this system, acetone as solvent of the starting material TCP is readily degraded to the primary product acetic acid[16,17] under the presence of oxidative species or radicals, thus it is understandable that some of coupling products (*e.g.*, B-4) can be found. Because the residues obtained from the zones were dissolved in CD_3COCD_3, all the deuterated products were formed through decomposition and exchange reaction only during MS measurements, which had no relation to the degradation process of TCP treated with air ions. Generally speaking, the dechlorinated intermediate products are more easily biodegradable[5]. 53% of the dechlorination ratio for TCP can be achieved after 60 min treatment with the present technique. So air ions generated by electric discharge can induce effective dechlorination, and might have a future in the oxidative removal of chlorinated phenols due to their simplicity and environmentally friendly behavior.

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