ISSN-1996-918X

Pak. J. Anal. Environ. Chem. Vol. 10, No. 1 & 2 (2009) 76-82

An Analytical Implication to Chlorides Determination in Catalytic Hydrodechlorination Reaction of DDT by Ion Chromatography

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Abstract

Chemical degradation of Organochlorine pesticide (OCPs) in hydrodechlorination reactions were first systematically investigated using *dichloro diphenyl trichloroethane* (DDT) as the model pesticide. The reaction of DDT produced an equimolar amount of HCl and DDE resulting from initial attack and was identified using GC-ECD. The produced DDE was dechlorinated by using Fe/Ni catalysts with a solution of NaOH in 2-propanol/methanol (99:1 v/v) at temperature below 82 ºC. The developed method efficiently converted DDT in the range of 3.5 – 3500 mg/l to chlorine-free product within 240 minutes. Chloride ions concentrations were also identified as a product using Ion Chromatography.

Keywords: Chloride, Hydrodechlorination, DDT, Organochlorine pesticides

Introduction

Deep- Safe disposal of OCPs is based on its detoxification. Disposal of OCPs has received noteworthy attention over the past several decades. Existing techniques for disposing of OCPs have been proposed including effective procedures such as high temperature incineration, chemical degradation and biological degradation. Chemical degradation have some advantages due to the higher rate of dechlorination over biological degradation [1] and other hand high temperature incineration that usually some noxious chemicals are released such as Dioxin [2-3].

Dehalogenation reactions have important synthetic and environmental potential and can be achieved by a variety of chemical methods. Hydrodechlorination is a class of dehelogenation reaction and is one of the most promising techniques for detoxification of organochlorine compounds [4].

Basically Pakistan is an agricultural country and mainly depends for its economy on crop production and it contributes 8% of the total global cotton production [5-6]. Pakistan mainly is an insecticide consumer country, the OCPs were previously extensively used in the cotton production and other agricultural activities and the use of pesticide has increased by 1169% in the last 20 years [7]. On the other hand at least three thousand metric tons of obsolete and expired pesticides have been stored under extreme hazardous conditions in more than thousand sites. Locally banned or severely restricted pesticides are easily available and DDT is continuously illegally imported and use in our country [8-10].

The aim of our study was to develop the cost effective and efficient method for the safe disposal of OCPs. This study is in continuation work on dechlorination of organochlorine pesticides (OCPs) with carbon supported transition metal catalysts in alkaline 2-propanol media.

Materials and Methods

The catalysts used in this study were Iron, Nickel and Cobalt metals obtained from Fisher Scientific Co., (USA). The catalysts which were powdered form pre-dried in a vacuum for 30 minutes at 200ºC and kept in a desiccator. 1,1-Bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT), 98% was purchased from Sigma-Aldrich Co., (USA). DDE (5000

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μg/ml), USEPA, standard also arranged, USA. 2-propanol (HPLC grade) was from Burdick & Jackson (USA). Methanol (100%), n-hexane (95 %), toluene and sodium hydroxide were from Mallinckrodt Baker, Inc. (USA). Activated carbon was from Calgon Carbon Co (USA). Water was deionized and purified by means of a Millipore-Q system USA. Na_2CO_3 and $NaHCO_3$ (AR grade, J.T Baker, USA) were used for preparation of eluent. DDT and the other standards were purchased form Acc Standard, USA. All chemicals and gases were high-purity grade and were used as obtained from suppliers without further purification.

Sample preparation

The degradation reactions were carried out in batch reactors. Two types of reactors were used for this study. First reactor 'R1' (without catalyst) was 50 ml pyrex glass tube (I.D = 10 mm, L = 100 mm) with screwed caped. The second reactor 'R2' (treated with catalyst) was 80 ml Pyrex glass tubes (I.D = 13 mm, L = 120 mm) with screwed caped. The tubes were washed with 20% nitric acid solution followed by Milli-Q water and dried in oven before the experiments. A water bath was used having heating capability along with sonication. The different concentrations of DDT (10, 1, 0.1, 0.01 mM) in 2-propanol and the different dilutions of NaOH (10, 25, 50, 75 mM) in 2-propanol / methanol (99:1 v/v) mixture were prepared. For initial experiments performed in R1 reactors with alkali.

Different combinations of catalysts are applied on dechlorination of 0.01 mM (3.5 ppm) DDT concentration in the presence of alkaline 2-propanol at temperature 80ºC for 12hr. In catalytic treatment the mixture of DDT and alkali solution were vortexes (900 rpm) at room temperature for 15 minutes. Small aliquots were removed and added to a toluene/water mixture (3:1 v/v, 2ml) and diluted for analysis by GC/ECD and IC. Then a catalyst (17-20 mg) was added and mixture was sonicated 12 hours and maintained at 80 ºC by means of a water bath. After the completion of the reaction, the reaction mixture was extracted with toluene/water mixture, followed by analysis of the liquid phases. The recovered catalyst was placed in an ultrasonic generator and extracted with 3 ml toluene. The concentration of DDT and products were determined by GC/ECD based on the responses of individual standards.

Different set of experiments were designed to study the effects of important variables (temperature, reaction time, alkali concentration) on hydrodechlorination of DDT with and without catalysts. Optimum conditions were applied on the different concentrations of DDT (0.01, 0.1 and 1.0 mM and high concentration 10 mM) along with successful catalysts. In another set of experiment solid DDT instead of liquid solution were treated.

Equipment

Gas chromatography analyses

DDT and partially dechlorinated product were analyzed using Hewlett-Packard GC-ECD instrument, equipped with Ni^{63} Electron Capture Detector and ZB-5 column (30m x 0.25 mm, 0.25 μm Film thickness). Injection was made in split-less mode using helium (He) as the carrier gas and temperature was set at 250 ºC. The GC oven temperature was held at 100 ºC with hold time for 10 minutes, ramped at 10 ºC/min to final temperature was set at 300 ºC. The detector temperature was set at 320 ºC. The flow rate was 1.5 ml/min.

End products were quantified from peak areas obtained through automated integration and also by comparison of standards.

Ion chromatography analyses

This investigation was carried out on an Ion Chromatograph System "ICS-2500" (Dionex CA, USA) consisting of a gradient pump (GP50), a conductivity detector (CD25A) and a suppresser (ASRS-4). The samples were injected through a 50 μl loop fitted to a Rheodyne six port injector. The separator column used was IonPac AS14, 250mm x 4mm with its guard column AG14 (Dionex CA, USA). The separation of the components is based on their specific affinity for the resin bed of the analytic column. Samples were run through Dionex AS50 automated sampler. Duplicate sample was analyzed after every five samples. To be considered acceptable, duplicate results were found within 0 and 3 standard deviations of the mean of the Relative Percent Difference (RPD). This value was not exceeded over 15%.

Calibration curve for analyte was plotted against the instrument response and standard concentration and computed the sample concentration by comparing the sample response with the standard curve. Results were multiplied by appropriate dilution factor (Calculations were done by Peaknet software). Results have been reported only for values those were fallen between the lowest and the highest calibration standards. Samples exceeding the highest standard were diluted and reanalyzed.

Quality control

Two quality control (QC) samples were used, one of them was in-house quality control sample prepared by the Environmental Laboratory Approval

Program (ELAP), USA and other one was an independent proficiency test sample, provided by Environmental Resource Associates (ERA), USA. A QC sample was analyzed every 5 samples as well as at the beginning and end of each batch run.

Result and Discussion

Batch experiments were carried out for the reactions of DDT with alkaline 2-propanol. When 10 ml of 0.01 mM concentration of DDT was treated with 0.1 ml of 100 mM alkaline 2-propanol at room temperature for 15 minutes, the transparent solution changed to cloudy white. Analysis of this solution by GC-ECD shows that the peak of DDT disappeared completely and a new intense peak was observed at shorter retention time. The new peak and DDE standard peak gave identical retention times. The mass balance between DDT and produced DDE during the reaction was maintained within experimental error. This indicates that one chlorine atom was released from DDT during this process and reacted with the proton from the OH group of 2-propanol to form HCl which was neutralized by the NaOH dissolved in the 2-propanol and finally converted into NaCl. As NaCl is insoluble in 2-propanol its formation in the solution gave a cloudy white appearance.

To achieve further dechlorination in DDT, different reaction conditions were applied. First, the effect of temperature was studied in the range of 40 to 80 °C and in the second step reaction time was set at 12 hr. and for every subsequent batch experiment; the reaction time was reached by an hour. The minimum reaction time was 0.5 hr. Concentration of both DDT and alkali in all experiments was same. The maximum temperature limit was fixed at 80 °C due to the boiling point of 2-propanol (b.p 82 °C). The results of first set of experiments show that in all samples, DDT was converted into DDE and temperature did not show any effect on further dechlorination Fig. 1. In other words reaction was found to be independent of temperature in the range of 40-80 °C. Results from the second set of experiments also showed similar DDT conversions as in case of temperature study in the first step, i.e. in all samples DDT was also converted to equivalent amount of DDE Fig. 2. It can be concluded based on these results that reaction was completed in less than 0.5 hr.

It is concluded from the results of these sets of batch experiments that treatment of DDT with alkaline 2-propanol only releases one chloride atom out of the five and gets converted into DDE, which is even more stable compound as compare to DDT. Further changes in reaction conditions (temperature and reaction time) could not dechlorinate more DDT. Therefore, it was decided to use catalyst to achieve further dechlorination. As catalysts are known to enhance the rate of reaction by lowering the activation energy. Transition metals are most widely studied as catalysts in hydrodehalogenation reactions and especially the 2nd and 3rd triads of group VIIIB elements are among the most frequently used. The selection of 1st triad of group VIIIB elements (Fe, Co, Ni) could be a good choice for our study because they are cheaper and have similar properties as compared to other triads (2nd and 3rd) of group VIII B transition elements.

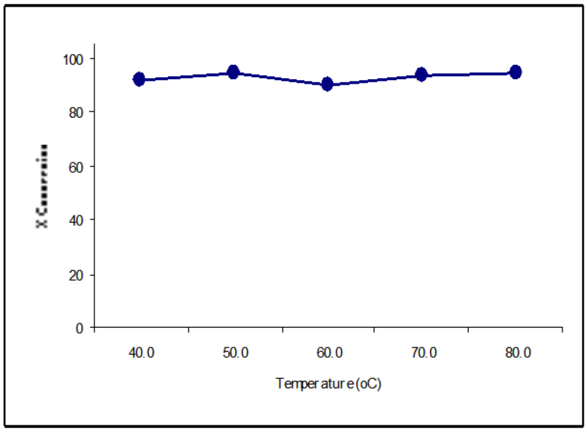

Figure 1. **Temperature profile for dechlorination of DDT into DDE. Reaction conditions: DDT, 0.01 mM; 2-propanol/methanol (99:1 v/v), 10ml; NaOH, 200mM, 0.1ml; reaction time 12 hr.**

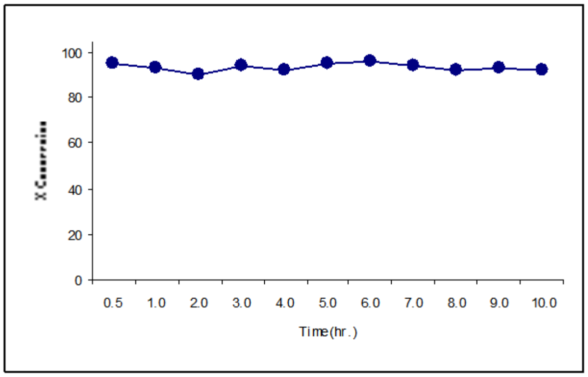

Figure 2. **Time profile for dechlorination of DDT into DDE. Reaction conditions: DDT, 0.01 mM; 2-propanol/methanol (99:1 v/v), 10ml; NaOH, 200mM, 0.1ml; temperature, 40 °C.**

Selected transition metals and their combination along with carbon support were used in hydrodechlorination reaction of DDT during the 12 hr. process. All parameter were initially set on higher side. The initial reaction time and temperature were set at 12 hr. and 80 °C. The concentration of DDT and alkaline 2-propanol were kept same, at 0.01 mM and 100 mM respectively. Although it was found previously that lower concentration of alkali (10 mM) could be used to dechlorinate one Cl^- ion from DDT. However, by using catalysts and higher concentration of alkali in dechlorination, more Cl$^-$ ions were expected to be released from DDT.

Different catalysts (Fe, Co, Ni) and their combinations (Fe/Co, Fe/Ni, Ni/Co and Fe/Co/Ni) were studied in the presence of alkaline 2-propanol/methanol (99:1 v/v) in dechlorination reactions. Results showed that the individual catalysts were not very effective for dechlorination but their combination showed better results. Of the various combinations of catalyst, the result from Fe/Ni was very promising Table-1. This combination was selected for further experiments.

Before proceeding to next step, we decided to study the extent of dechlorination by using Fe/Ni combination catalyst in the absence of NaOH, to investigate the cost effectiveness of the overall process. The reactions conditions were kept similar. The results of GC/ECD and IC showed that the combination of Fe/Ni was not effective and at the same time the reaction rate was very slow Table-2. After 12 hr. only 11% of DDT was converted to DDE. In order to check the effectiveness of this combination for indefinite time (~ 2 weeks) in absence of NaOH, same batch experiment under similar reaction conditions were carried out. Even after 72 hr. the percentage of dechlorination achieved could not exceed more than 12%. This may be due to the poising of the catalyst surface itself and thus limiting the capability of using Fe/Ni combination alone for dechlorination.

Table 1. **The effect of different catalysts and their combination on DDT (0.01 mM) treatment reaction at constant temperature (80 ^{o}C) and reaction time (12 hr) in alkaline 2-porpanol (100 mM).**

Sample I.D	DDT Conc. (0.01 mM) (mg/l)	Catalyst used	Ret. Time (min)	Obs. Value (mg/l)	Dil. Factor	Final Result (mg/l)	Conversion in DDE (%)	Dechlorination of Cl$^-$ in DDT (%)
GC-ECD analysis results				**DDE**				
DDT-22	3.545	Fe	24.483	2.855	1.0	2.860	92	
DDT-23	3.545	Co	24.465	2.892	1.0	2.800	94	
DDT-24	3.545	Ni	24.478	2.897	1.0	2.900	90	
DDT-25	3.545	Fe/Co	24.482	2.762	1.0	2.760	93	
DDT-26	3.545	Fe/Ni	n.a	BDL	1.0	n.a	BDL	
DDT-27	3.545	Co/Ni	24.465	2.872	1.0	2.870	94	
DDT-28	3.545	Fe/Co/Ni	n.a	BDL	1.0	n.a	BDL	
IC analysis results				**Chloride**				
DDT-22	3.545	Fe	2.14	1.345	2.5	3.36		19.0
DDT-23	3.545	Co	2.11	0.922	2.5	2.30		13.0
DDT-24	3.545	Ni	2.15	0.743	5	3.72		21.0
DDT-25	3.545	Fe/Co	2.17	1.274	2.5	3.19		18.0
DDT-26	3.545	Fe/Ni	2.12	6.742	2.5	16.86		95.1
DDT-27	3.545	Co/Ni	2.12	0.780	2.5	1.95		11.0
DDT-28	3.545	Fe/Co/Ni	2.13	6.792	2.5	16.98		95.8

***BDL** = Below detectable limit; **n.a** = not applicable*

Table 2. **The effect of Fe/Ni catalysts without alkali on DDT (0.01 mM) treatment reaction at constant temperature (80 ^{o}C) and reaction time (12 hr) in 2-porpanol(100 mM).**

Sample I.D	DDT Conc. (0.01 mM) (mg/l)	Catalyst used	Ret. Time (min)	Obs. Value (mg/l)	Dil. Factor	Final Result (mg/l)	Conversion in DDE (%)	Dechlorination of Cl$^-$ in DDT (%)
GC-ECD analysis results				**DDE**				
DDT-29	3.545	Fe/Ni	24.449	0.389	1.0	0.390	11	
IC analysis results				**Chloride**				
DDT-29	3.545	Fe/Ni	2.15	0.920	2.5	2.30		13.0

From this batch experiments it may be concluded that the use of NaOH is important during dechlorination. As Fe/Ni catalyst combination was very effective in dechlorination, the reaction conditions in alkaline 2-propanol were optimized with respect to reaction time and temperature. In first set of experiments reaction time was varied from 12 -2 hr; for second set of experiments the temperature was varied in the range of 80-40 °C. The results from these two sets of experiments showed that maximum dechlorination occurred at the reaction time of 4 hr. and temperature of 80 °C Fig. 3 and 4 and thus were chosen as optimum conditions for this process.

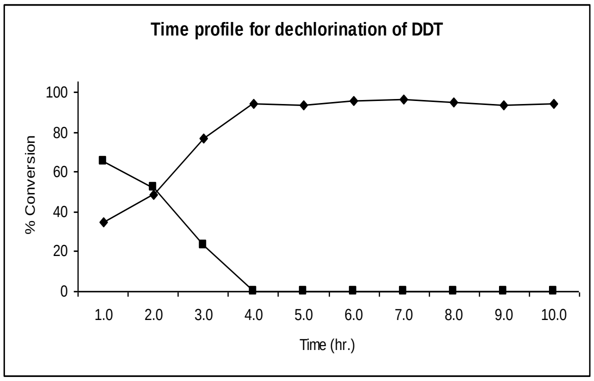

Figure 3. **Time profiles for Catalytic dechlorination of DDT with Fe/Ni at 80 °C in 2-propanol/methanol (99:1 v/v), 10ml; NaOH, 200mM, 0.1ml. DDE was produced by treating DDT with NaOH.**

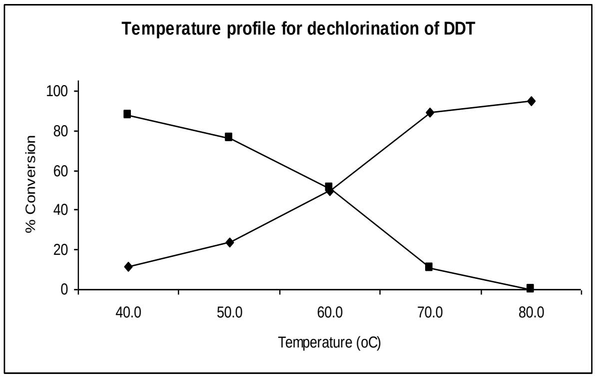

Figure 4. **Temperature profiles for Catalytic dechlorination of DDT with Fe/Ni in 2-propanol/methanol (99:1 v/v), 10ml; NaOH, 200mM, 0.1ml; reaction time 4 hr. DDE was produced by treating DDT with NaOH.**

After successful selection of catalyst combination and optimizing the reaction conditions, the method developed was then applied to different concentrations of DDT from low (0.01 mM) to high concentration (10mM). Another set of experiment was designed in which instead of liquid solution, solid DDT was used, to check whether this method may be directly applied to both liquid and solid phases. Results showed that the method was effective for dechlorination of both the liquid as well as solid DDT over the wide concentration range Table-3 and 4.

Table 3. **The hydrodechlorination treatment on different DDT concentrations at constant temperature (80 °C) for 4 hr.**

Sample I.D	Conc. of DDT (mM)	(mg/l)	Ret. Time (min)	Obs. Value (mg/l)	Dil. Factor	Final Result (mg/l)	Conversion in DDE (%)	Dechlorination of Cl^- in DDT (%)
GC-ECD analysis results					**DDE**			
DDT-47	0.01	3.54	n.a	BDL	1.0	n.a	BDL	
DDT-48	0.1	35.45	n.a	BDL	1.0	n.a	BDL	
DDT-49	1.0	354.5	n.a	BDL	1.0	n.a	BDL	
DDT-50	10.0	3544.9	n.a	BDL	1.0	n.a	BDL	
IC analysis results					**Chloride**			
DDT-47	0.01	3.54	2.12	6.714	2.5	16.79		94.7
DDT-48	0.1	35.45	2.17	8.313	20	166.3		93.8
DDT-49	1.0	354.5	2.12	1.675	1000	1675.0		94.5
DDT-50	10.0	3544.9	2.13	1.108	15000	16625.6		93.8

***BDL** = Below detectable limit; **n.a** = not applicable*

Table 4. **The hydrodechlorination treatment on high DDT concentrations at constant temperature (80 ºC) for 4 hr.**

Sample I.D	**Conc. of DDT** (mM)	**Conc. of DDT** (mg/l)	**Ret. Time** (min)	**Obs. Value** (mg/l)	**Dil. Factor**	**Final Result** (mg/l)	**Conversion in DDE** (%)	**Dechlorination of Cl^- inDDT** (%)
GC-ECD analysis results			**DDE**					
DDT-51	10	3544.9	n.a	BDL	1.0	n.a	BDL	
DDT-52	10	3544.9	n.a	BDL	1.0	n.a	BDL	
DDT-53	10	3544.9	n.a	BDL	1.0	n.a	BDL	
DDT-54	10	3544.9	24.402	1.949	10.0	19.49	0.6	
IC analysis results			**Chloride**					
DDT-51	10	3544.9	2.12	1.134	15000	17015.5		96.0
DDT-52	10	3544.9	2.12	1.230	15000	16838.3		95.0
DDT-53	10	3544.9	2.12	1.123	15000	16838.3		95.0
DDT-54	10	3544.9	2.44	1.052	15000	15774.8		89.0

BDL *= Below detectable limit;* ***n.a*** *= not applicable*

Proposed pathway

$$Fe^0 \longrightarrow Fe^{+2} + 2e^- \qquad (1)$$

$$H^+ + e^- \xrightarrow{Ni} H^* \qquad (2)$$

$$CH_3CH(OH)CH_3 \longrightarrow CH_3C(O)CH_3 + 2H^* \qquad (3)$$

Equations (4-6) show the proposed pathway for dechlorination of DDT by means of a stoichiometric reaction with NaOH and a catalytic reaction with Fe/Ni.

$$Ni\text{-}H + C_{14}H_9Cl_5 \longrightarrow Ni\text{-}Cl + C_{14}H_8Cl_4 \qquad (4)$$

$$Ni\text{-}Cl + H_2 \longrightarrow Ni\text{-}H + HCl \qquad (5)$$

$$HCl + NaOH \longrightarrow NaCl + H_2O \qquad (6)$$

This above proposed mechanism indicates that hydrodechloriantion and deactivation process take place simultaneously. Poising of the metal surface depends on the equilibrium between poisoning and regeneration of Ni surface. In the catalytic reaction the solvent serves as the hydrogen source in removal of chorines and hydrogenation of a double bond between aliphatic carbons.

Conclusion

Different catalysts were studied for the hydrodechlorination of DDT. The reactions were run with different concentrations of DDT and either in presence or in the absence of alkaline solvent system. The products were monitored by traditional method GC/ECD and used a new approach for chloride measurement by IC which indicated the dechlorination. DDT released an equimolar amount of HCl and was transformed to DDE by stoichiometric reaction with NaOH and then this intermediate product DDE dechlorinated stepwise to chlorine–free product over Fe/Ni.

We also demonstrated that 10 mM (3550 mg/L) of these highly persistent and stable DDT can be complete dechlorinated to a chlorine–free product at temperatures below 82 ºC in 2-propanol /methanol (99:1 v/v) in the presence of NaOH and Fe/Ni within 4 hrs.

This developed catalytic hydrodechlorination method is cost effective which to be employed for degradation of hazardous chlorinated aromatics and aliphatics.

Acknowledgments

The author is grateful to Dr. Haider A. Khwaja and Dr. Mirza Hussain, Dept. of Environmental Health Sciences, School of Public Health, University at Albany, NY, USA, for their technical support. Author would also like to thank Wadsworth Center, State Department of Health, New York, USA for allowing me to use their facilities.

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