Electroreduction of Polychlorobenzenes Using Either Lead or Copper Electrodes

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Polychlorobenzenes can be reduced electrolytically to dichlorobenzenes by using either lead or copper as the electrodes in a MeOH/THF solution. Among the resultants of dichlorobenzenes, 1,4-dichlorobenzene is a major product that might be due to a low enthalpy of formation. A chlorine atom situated at the ortho position of another chlorine atom in the benzene ring is removed prior to others. However, the sequence of reactivities of the polychlorobenzenes for electroreducing by lead electrodes in this study is as follows: 1,2,3,4-$C_6H_2Cl_4$ > 1,3,5-$C_6H_3Cl_3$ > C_6HCl_5 ~ 1,2,4,5-$C_6H_2Cl_4$ > 1,2,3,5-$C_6H_2Cl_4$ ~ 1,2,3-$C_6H_3Cl_3$ > 1,2,4-$C_6H_3Cl_3$ > C_6Cl_6.

Diverse organic chlorides, which are wide industrial useful but toxic and non-biodegradable, have been widely used as organic solvents, pesticides, and transformer oils, etc. Numbers of those compounds are stable under ambient conditions and are classified as persistent organic pollutants (POPs). The process that converts those compounds into less toxic structures or renders them biodegradable is a crucial issue in environmental remediation. Hydrodehalogenation of aromatic chlorides has been intensively studied by using chemical reduction,[1] electroreduction,[2] photodegradation,[3] and degradation using microorganisms.[4] Inherent advantages of the cathodic dehalogenation are: (a) treatment at ambient temperature and (b) selective removal of chloride while the organic skeleton remains to be digested by the biological route.[5] This method is often cheap, technically flexible and readily allows dechlorination of different chlorinated organic compounds. However, no work has been reported in detail regarding dechlorination of polychlorobenzenes. In the present study, we attempt to search for the dissolvable electrodes in order to remove the chlorine atom from polychlorobenzenes. The initial rates for electrodechlorination of the various polychlorobenzenes in the presence of $LiClO_4$ as an electrolyte are also investigated.

RESULTS AND DISCUSSION

The solubilities of the polychlorobenzenes in MeOH decrease upon the increase of the chlorine atoms on the benzene. THF is added to MeOH as a cosolvent to enhance the solubilities of polychlorobenzenes. Even in the MeOH/THF (1:1 volume ratio) solution, low solubility of hexachlorobenzene leads to presence of suspension solid in this study. Carbon fiber, graphite, magnesium, aluminum, copper, and lead were applied as the electrodes to examine their ability to remove chlorine atoms. During the electrolysis, an alternative polarity on electrodes (change every 30 sec) was applied to avoid electrodeposition on the electrodes. Among them, carbon fiber and graphite are unable to remove any of the chlorine atoms from pentachlorobenzene under 15 V applied voltage; however, magnesium and aluminum are readily dissolved in MeOH/THF during electrolysis to form the collide resultants. Lead and copper electrodes demonstrate their ability to remove chlorine atoms from polychlorobenzenes. However, the dichlorobenzenes are intact during electrolysis under the same conditions for more than 600 min.

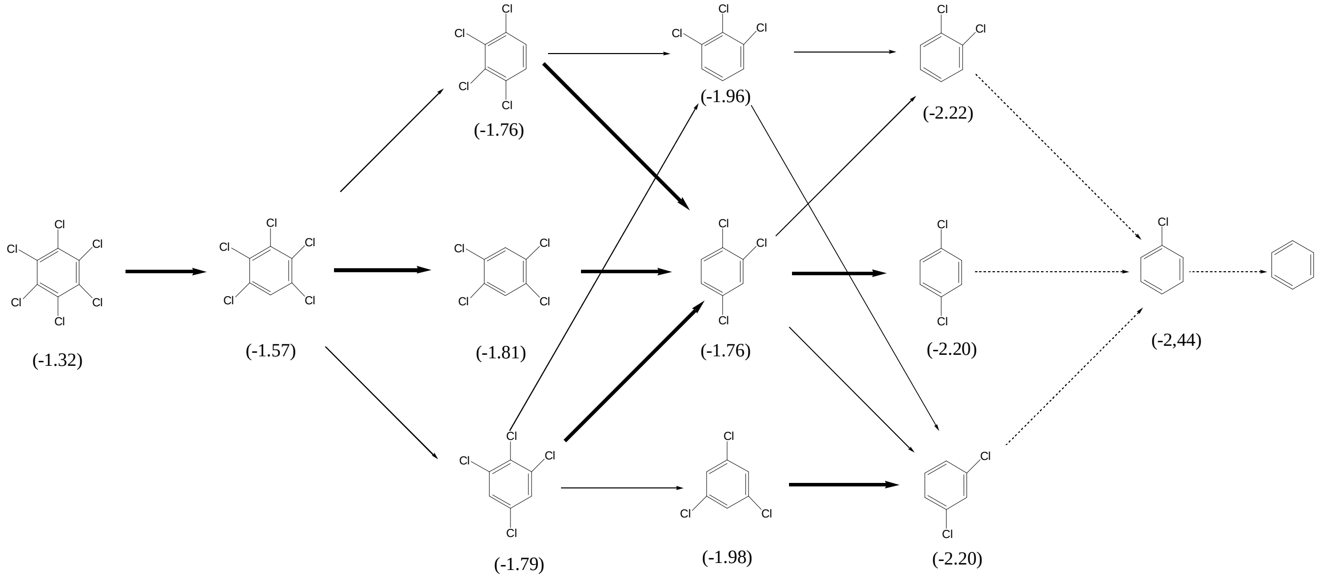
The reaction rates of electrodechlorination of eight polychlorobenzenes using copper and lead electrodes are summarized in Table 1. The copper electrodes displayed less activities to remove chlorine atoms from tri- and tetrachlorobenzenes than lead electrodes, while the reaction rates were comparable to lead in the case of penta- and hexa-chlorobenzene. Therefore, the lead electrodes were used for this study. The amount of current depended on the concentration of electrolytes. High concentration of electrolyte provides more ionic species and forms high current density. Higher current density produced more electron flow for the reduction of polychlorobenzenes and led to higher reaction rates (Table 1) as well as generating more heat. The concentrations of $LiClO_4$ of 30 mM were used for this study. The relative reaction rates and the half-wave potentials for chlorinated benzenes are summarized in Scheme I, where the larger ar-

Table 1. Rate of Hydrodechlorination of Polychlorobenzenes in MeOH/THF Function on the Concentration of $LiClO_4$[a]

Electrode	$LiClO_4$ (mM)	reactants							
		1,2,3-$C_6H_3Cl_3$	1,2,4-$C_6H_3Cl_3$	1,3,5-$C_6H_3Cl_3$	1,2,3,4-$C_6H_2Cl_4$	1,2,3,5-$C_6H_2Cl_4$	1,2,4,5-$C_6H_2Cl_4$	C_6HCl_5	C_6Cl_6
Cu	10	0.008±0.002	0.004±0.001	0.007±0.002	0.015±0.004	0.020±0.003	0.010±0.002	0.030±0.003	0.016±0.002
Pb	10	0.032±0.004	0.023±0.004	0.042±0.003	0.047±0.003	0.033±0.003	0.037±0.003	0.037±0.002	0.020±0.003
Pb	30	0.078±0.004	0.057±0.004	0.070±0.004	0.110±0.007	0.072±0.004	0.071±0.003	0.070±0.003	0.062±0.002
Pb	50	0.102±0.006	0.072±0.003	0.103±0.008	0.147±0.006	0.110±0.006	0.090±0.002	0.150±0.004	0.115±0.008

[a] Reactant (10.0 mmol), internal standard (n-dodecane, 5.0 mmol) in 100 mL (50/50: MeOH/THF) solution, initial electrode area in the solution is 100 mm^2, the average reaction rates (mM/min) were determined at first 10% consumed from three experiments.

Scheme I Relative rates of electrolytic dechlorination of polychlorobenzenes. The heavier arrows indicate higher rates in that pathways and the dotted arrows indicate no reaction in that pathway. The values in the parenthesis represented the half-wave potentials[9]



rows represent the higher initial rates. According to the literature, the half-wave potentials were obtained by cyclic voltametry in 0.1 M $(C_2H_5)_4N^+Br^-$ in dimethylsulfoxide. The reduction potentials were determined from the differential *i*-E curve against SCE.[9] From the scheme, we could find that the initial rates for removing the chlorine atom from chlorinated benzenes strongly depended on the half-wave potentials. The half-wave potentials for dichlorobezenes and chlorobenzene are smaller than -2.00 volts and were inert during the electroreduction in this study.

The progress of reactions were monitored by GLC analyses. Under our analytic conditions, all the chlorinated benzenes along with n-dodecane were well separated except for 1,2,3,5- and 1,2,4,5-tetrachlorobenzenes (Fig. 1). In this circumstance, only an uncertainty could be encountered in the electrolysis of pentachlorobenzenes. The amounts of consumed polychlorinated benzenes were in balance with those of the products, indicating that stoichiometric dechlorination occurred in this system. No other by-products other than the partially dechlorinated benzene derivatives were detected, indicating that this electrochemical reaction was very selective. The product distributions from electrolytic hydrodechlorination of polychlorobenzenes for 300 min are summarized in Fig. 1 using bar graphics. It is found in the figure that the predominant products were 1,4-dichlorobenzene derivatives and 1,2,4-trichlorobenzene derivatives, suggesting the formation of common intermediates in the dechlorination process for electrochemical systems.

During the electrolysis of trichlorobenzenes, 1,3-dichlorobenzene was formed as the sole product from 1,3,5-troichlorobenzene, while 1,4-dichlorobenzene formed as a major with 1,3-dichlorobenzene as a minor, and 1,3-dichlorobenzene formed as the major with 1,2-dichlorobenzene as a minor for 1,2,4-, and 1,2,3-trichlorobenzenes, respectively. In the latter two cases, it is suggested that the chlorine atoms possessing a chlorine atom at the *ortho*-position will be activated by each other. Although a chlorine at position-2 of 1,2,3-trichlorobenzene will have more steric hindrance than others and with 1/3 possibility compared to the 2/3 possibility for others by accounting for the number of atoms, it seems to be more likely due to the activation by two chlorine atoms. This activation phenomenon is the same as the observation from electrolysis of polyfluorobenzenes using mercury electrodes.[6]

The chlorine possessing an ortho-chlorine atom is more easily removed as the situation of trichlorobenzenes is also observed in the tetrasubstituted compounds. That 1,4-dichlorobenzene was formed along with the formation of 1,2,4-trichlorobezene during electrolysis of 1,2,3,4-tetrachlorobenzene might suggest that two chlorine atoms were removed before the chlorinated benzenes desorbed from the electrodes. (Fig. 3) The same reaction results were reported on dechlorination of 1,2,3,4-tetrachlorobezene photocatalyzed by ZnS under UV light.[7] According to the product distribution patterns from electrolysis of 1,2,3-trichlorobenzenes, dechlorination of 1,2,3,5-tetrachlorobenzenes may yield the production of 1,3,5-trichlorobenzene. (Fig. 4) However, a chlorine atom is able to activate the *meta*-position, an electrophilic substitution of benzene ring, to form 1,2,4-trichlorobenzene as an initial product.

Electrolysis of pentachloro- and hexachlorobenzenes led to the same product distribution, while 1,2,4,5-tetrachloro- and 1,2,4-trichlorobenzenes were formed at the initial time and 1,4-dichlorobenzene was a final product. (Figs. 5, 6) Electrolysis of hexachlorobenzene led to 1,2,4-trichlorobenzene and 1,2,4,5-tetrachlorobenzene as the initial products followed by formation of 1,4-dichlorobenzene. No pentachlorobenzene observed from GC analysis with formation of trichlorobenzene as an initial product might indicate that the polychlorobenzenes are absorbed on the electrode surface and can remove more than two chlorine atoms before being desorbed by changing the electrode polarity. Penta- and hexachlorobenzene were selectively and stepwise dechlorinated to form less-chlorinated homologues, through tetrachlorobenzene, and trichlorobenzene to dichlorobenzene as the final products.

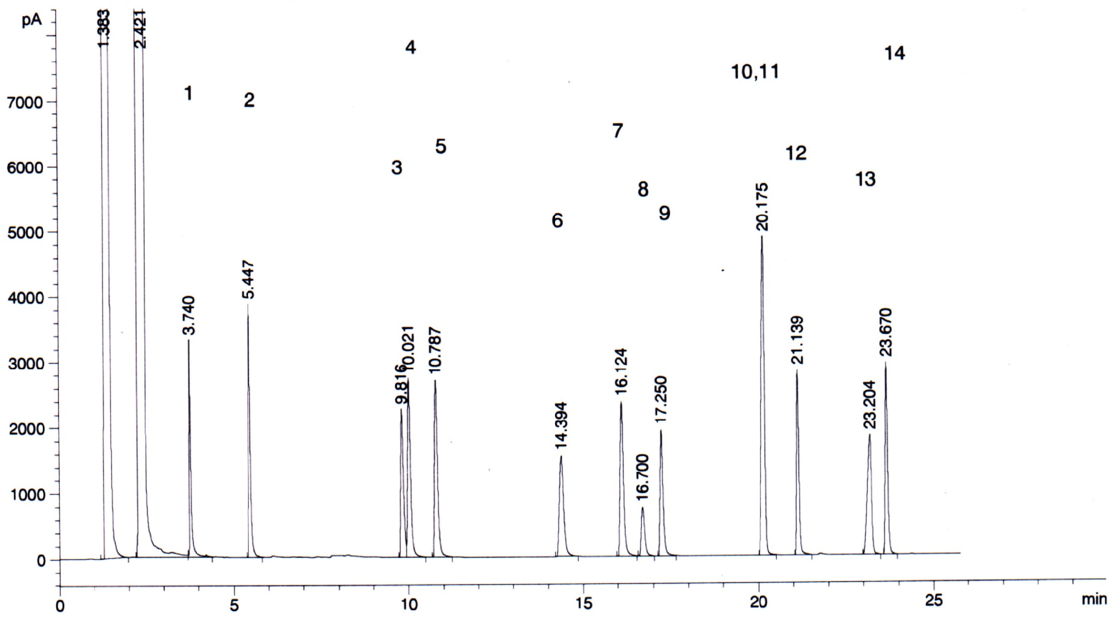


Fig. 1. Chlorinated benzenes were analyzed by gas chromatography (Hewlett Packard 6890 Series with the autosampler; column: Alltech ECONOCAP$^{\text{TM}}$ #19657 SE-54, 30 m length, 0.53 mm i.d. with 1.2 μm film thickness and FID). The flow rate of the carrier gas (nitrogen) was 26.3 mL/min, the temperature program started at 50 °C (constant for 3 min), ramped at 5 °C/min up to 110 °C (constant for 3 min), at 3 °C/min up to185 °C (constant for 1 min), and at 60 °C/min up to 200 °C. (1) toluene; (2) monochlorobenzene; (3) 1,3-dichlorobenzene; (4) 1,4-dichlorobenzene; (5) 1,2-dichlorobenzene; (6) 1,3,5-trichlorobenzene; (7) 1,2,4-trichlorobenzene; (8) n-dodecane; (9) 1,2,3-trichlorobenzene; (10,11) 1,2,3,5-tetrachlorobenzene+1,2,4,5-tetrachlorobenzene; (12) 1,2,3,4-tetrachlorobenzene; (13) pentachlorobenzene; (14) hexachlorobenzene.

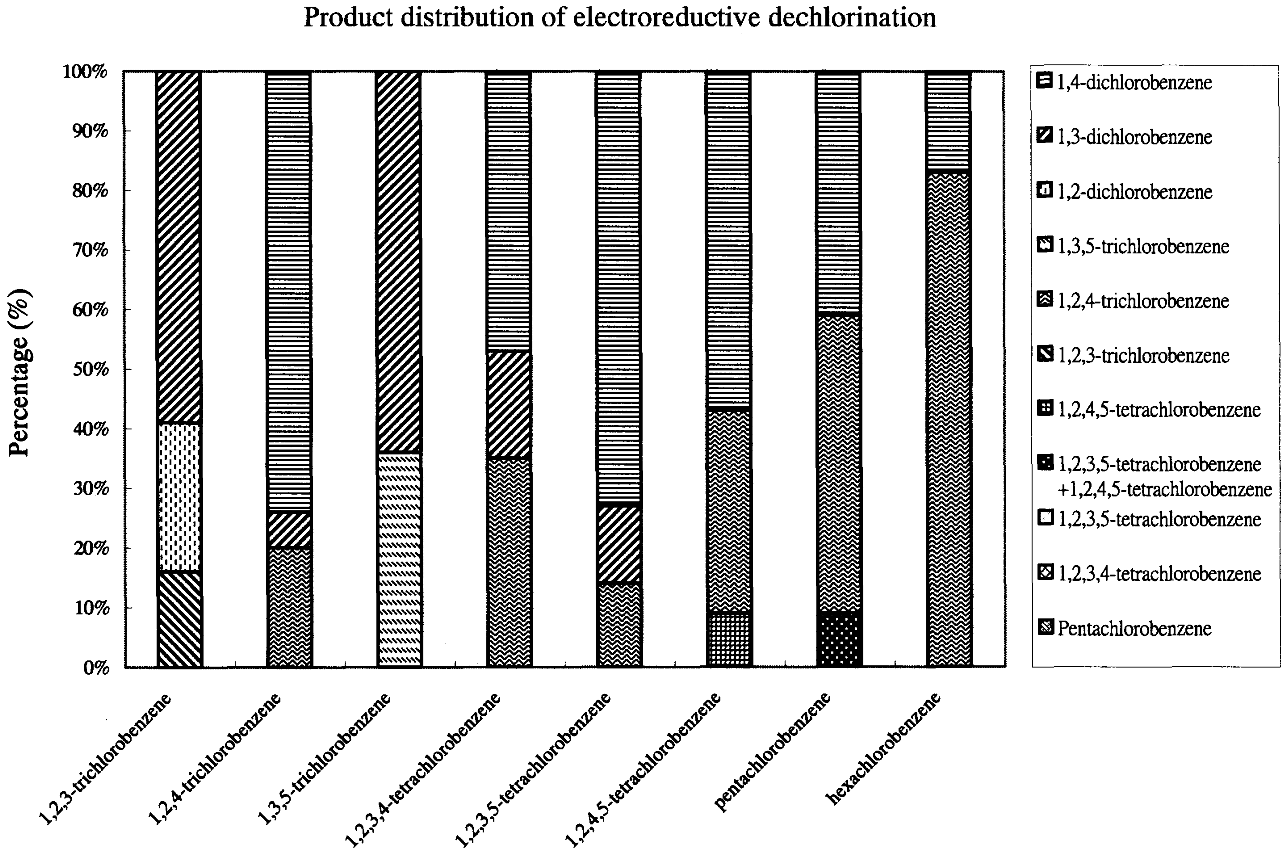


Fig. 2. Product distribution from electroreductive dechlorination of various polychlorobenzenes for 6 hrs on lead cathode in the solution containing 30 mM $LiClO_4$ as an electrolyte (current density = 10 mA/mm^2).

CONCLUSION

During the electrolysis of polychlorobenzenes, the activities of chlorinated benzenes toward electroreduction depended on their half-wave potentials. The half-wave potentials must be larger than -2.00 volt for the reduction to take place. That 1,4-dichlorobenzene is always formed as a final product might be due to the lowest enthaphy of formation among three isomers (7.89, 6.72, and 5.88 Kcal/mol for 1,2-, 1,3-, 1,4-dichlorobenzene, respectively)[8] which, in turn, indi-

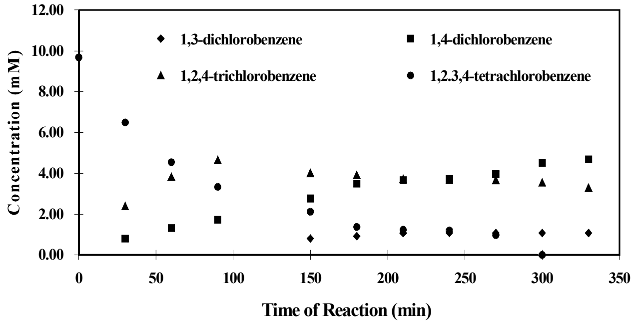


Fig. 3. Electroreductive dechlorination of 1,2,3,4-tetrachlorobenzene on lead plate cathode in the solution containing 30 mM $LiClO_4$ as an electrolyte.

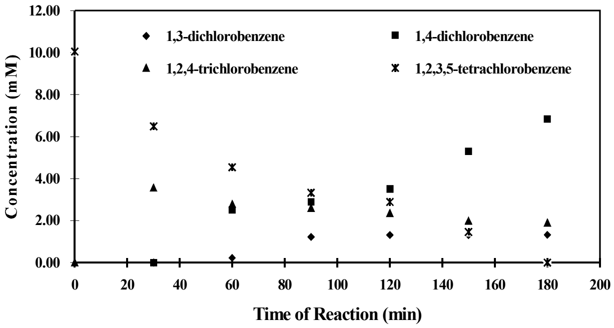


Fig. 4. Electroreductive dechlorination of 1,2,3,5-tetrachlorobenzene on lead plate cathode in the solution containing 30 mM $LiClO_4$ as an electrolyte.

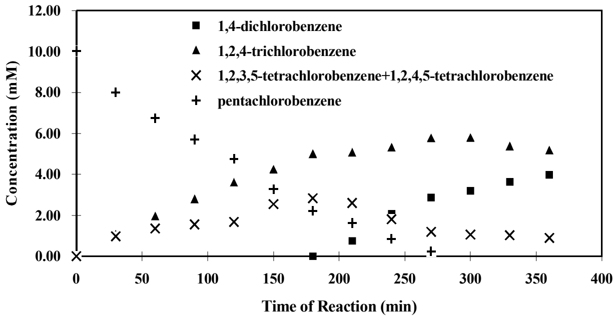


Fig. 5. Electroreductive dechlorination of pentachlorobenzene on lead plate cathode in the solution containing 30 mM $LiClO_4$ as an electrolyte.

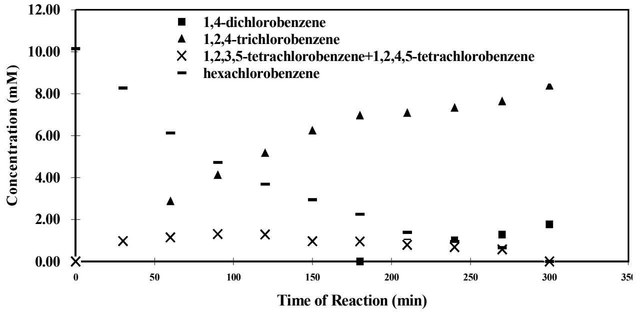


Fig. 6. Electroreductive dechlorination of hexachlorobenzene on lead plate cathode in the solution containing 30 mM $LiClO_4$ as an electrolyte.

cates a thermodynamic control process is operated for the product distribution. Strong absorption of polychlorobenzenes by electrodes lead to more than two chlorine atoms being removed before the products desorbed during the change of electrode polarity.

EXPERIMENTAL

Electrolysis of Polychlorobenzenes

Typical procedure (precautions must be taken against spark formation of locate overheating caused by faulty electrical connections. During electrolysis, potential explosive mixtures of gases may be formed (H_2, O_2, Cl_2 etc.). Protective measures must be taken to eliminate the danger of explosions. Dried perchlorates are potential explosive compounds; overheating a mixture containing perchlorate must be avoided. All reactions were performed in an undivided glass cell with a magnetic stirrer and a water-circulation system to control the temperature at 25 ± 3 °C. Solutions of polychlorobenzene, n-dodecane (as internal standard) and $LiClO_4$ were well mixed by means of ultrasonic irradiation for 5 min before electrolysis. The electrodes were polished with sandpaper (400 mesh) and then washed with water, acetone, and followed by drying. The terminal potential of 15 volts was applied on a pair of lead electrodes (10 mm × 1 mm × 40 mm, distance between two electrodes 2.0 cm, surface area immersion in the solution about 400 mm^2) and the electrode polarities were changed every 30 sec. The aliquots (1.0 mL) were sampled for tracing the progress of reactions every 30 min. The samples were directly analyzed with a Hewlett Packard 6,890 series II gas chromatograph (column Alltech Econo-Cap^{TM} SE-54, 30 m × 0.53 m × 1.2 μm film thickness). The flow rate of the carrier gas (nitrogen) was 26.3 mL/min; the temperature program started at 50 °C, (held for 3 min), heated at 5 °C /min to 110 °C, (held for 3 min), heated at 3 °C /min to 185 °C, (held for 1 min), heated to 200 °C, (held for 1 min). The product ratios were calculated based on the peak areas and corrected with response factors of products. The injector and the FID detector were held at 250 °C. A Finnigan MD-800 GC/MS was used to confirm peak identity. The reaction rates were measured according to the diminishing of reactant at first 10% consumption.

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Key Words

Electroreduction; Polychlorobenznes; Lead electrodes; Copper electrodes; Relative initial rates.

REFERENCES

1. (a) Oku, A.; Yasufku, K.; Kataoka, H. *Chem. Ind.* **1978**, *21*, 841. (b) Epling, G. A.; Florio, E. M. *J. Chem. Soc. Perkin Trans. 1* **1988**, 703. (c) Epling, G. A.; Florio, E. M.; Bourque, A. J.; Qian, X.-H.; Stuart, J. D. *Environ, Sci. Technol.* **1988**, *22*, 952. (d) Roth, J. A.; Dakoji, R. C.; Hughes, R. C.; Carmody, R. E. *Environ. Sci. Technol.* **1994**, *28*, 80.
2. (a) Sonoyama, N.; Sakata, T. *Environ. Sci. Technol.* **1998**, *32*, 4005. (b) Tsyganok, A. I.; Otsuka, K. *Electrochimica Acta,* **1998**, *43*, 2589. (c) Merica, S. G.; Jedral, W.; Lait, S.;

Keech, P.; Bunce, N. J. *Can. J. Chem*. **1999**, *77*, 1281. (d) Nünnecke, D.; Voss, J. *Acta Chemica Scand*. **1999**, *53*, 824. (e) Petersen, D.; Lemmrich, M.; Altrogge, M.; Voss, J. *Z. Naturforsch*, **1990**, *45b*, 1105.

3. (a) Chu, W. *Environ. Sci. Technol*. **1999**, *33*, 421. (b) Betterton, E. A. *Environ. Sci. Technol*. **2000**, *34*, 1229.
4. (a) Øfjord, G. D.; Puhakka, J. A.; Ferguson, J. F. *Environ. Sci. Technol*. **1994**, *28*, 2286. (b) van Dort, H. M.; Smullen, L. A.; May, R. J.; Bedard, D. L. *Environ. Sci. Technol*. **1997**, *31*, 3300. (c) Carr, C. S.; Garg, S.; Hughes, J. B. *Environ. Sci. Technol*. **2000**, *34*, 1088. (d) Wu, Q.; Bedard, D. L.; Wiegel, J. *Environ. Sci. Technol*. **1999**, *33*, 595.
5. (a) Gassman, J.; Vess, J.; Adiwidja, G. *Z. Naturforsch*, **1995**, *50b*, 953. (b) Zhang, S.; Rusding, J. F. *Environ. Sci. Technol*. **1995**, *29*, 1195. (c) Kulikov, S. M.; Plekhanov, V. P.; Tsygenok, A. L.; Schimm, C.; Heitz, E. *Electrochim. Acta*. **1996**, *41*, 527. (d) Cheng, J. F.; Fernando, D.; Corte, N. *Environ. Sci. Technol*. **1997**, *31*, 1074.
6. Tezuka, M.; Iwasaki, M. International Symposium on Organic Reaction, Tainan, Taiwan, **1993**, p 129.
7. Yin, H.; Wada, Y.; Kitamura, T.; Yanagida, S. *Environ. Sci. Technol*. **2001**, *35,* 227.
8. Platonov, V. A.; Simulin, Y. N. *Russ. J. Phys. Chem. (Engl. Transl.)* **1983**, *57*, 840.
9. Komenda, J.; Janderka, P. *Collect. Czech. Chem. Commun*. **1979**, *44*, 1715.