

Complete Dechlorination of Chlorinated Aromatic Compounds by Electrochemical Reduction with Naphthalene Radical Anion as Mediator

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It is widely known that electrochemical reduction offers one of effective methods for the dechlorination of chlorinated organic compounds. Many papers have been published concerning the reaction mechanism, most of which were studied by cyclic voltammetry¹. However it is not yet clear whether it is a practically useful method. For toxic and persistent chlorinated compounds such as PCBs and PCDD/Fs, complete dechlorination is necessary from a point of view of environmental protection. Authors investigated the possibility of electrochemical reduction for the complete dechlorination of chlorinated aromatic compounds.

Reaction conditions were searched using 1-chloronaphthalene as a substrate. Among various factors including electrode materials, supporting electrolytes and solvents, we selected glassy carbon, tetra-n-butyl-perchlorate and dimethylformamide (DMF) because stable potential or current was obtained. Even in this system, it was difficult to get enough current for continuation of reaction at the potential of substrate reduction, possibly because of passivation of electrode. Enough current was obtained at the reduction potential of naphthalene, a product of dechlorination, and complete (>99.99%) dechlorination was achieved. It was considered that naphthalene was reduced to radical anion, and its large reduction power enabled the rapid dechlorination. Radical anion of aromatic compounds is often used as mediator in electrochemical reduction but mostly in catalytic amount and at more positive potential than that of substrate. In our system, the concentration of naphthalene increases during reaction and the potential is more negative than substrate. Furthermore, it was found the reaction rate was accelerated by the use of excess amount of naphthalene from the initial point of reaction (Figure 1). Current efficiency was more than 100% with the assumption of 2-electron process. The effect of the concentration of naphthalene and substrate was kinetically investigated. The reaction rate increased proportionally to the concentration of naphthalene, whereas the order of reaction was 0.5 for the substrate concentration. By the use of excess amount of naphthalene, complete dechlorination was possible even if water content is 1%.

The same approach was applied for the dechlorination of PCB. Large reaction rate could be obtained for complete decomposition, using excess amount of biphenyl or naphthalene as mediator (Figure 2). Naphthalene was preferred because of less side reaction. Although the dechlorination is considered to proceed stepwise, few intermediates of lower chlorine number were detected during the reaction. Also, the difference in reactivity between congeners was not observed. These results show the reaction to be very rapid. Anthracene or diphenylanthracene, which were used by Connors et al.², was also examined. Reduction potential was more positive with these mediators, but the reaction rate was not sufficient for complete dechlorination and a lot of intermediates were detected. The effect of the concentration of naphthalene and substrate was investigated and found to be similar to the case of 1-chloronaphthalene.

In conclusion, electrochemical reduction with electrochemically generated naphthalene radical anion was confirmed to offer a rapid and complete method for the dechlorination of PCBs and related compounds.

References

1. D. G. Peters In Organic Electrochemistry; H. Lund, O. Hammerich, Eds.; Marcel Dekker: New York, 2001, pp 341-377.
2. T.F. Conors, J.F. Rusling J.Electrochem. Soc. 1983, 130, 1120-1121.

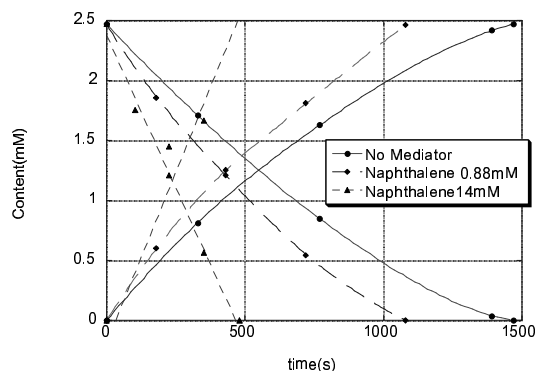


Figure 1. Change in content of 1-chloronaphthalene (descending) and naphthalene (ascending) with and without mediator addition

Electrode: Glassy carbon plate
Initial content of 1-chloronaphthalene: 2.47 mM
0.1 M tetra-n-butylammonium perchlorate in DMF
-3000 mV vs. Ag/Ag+

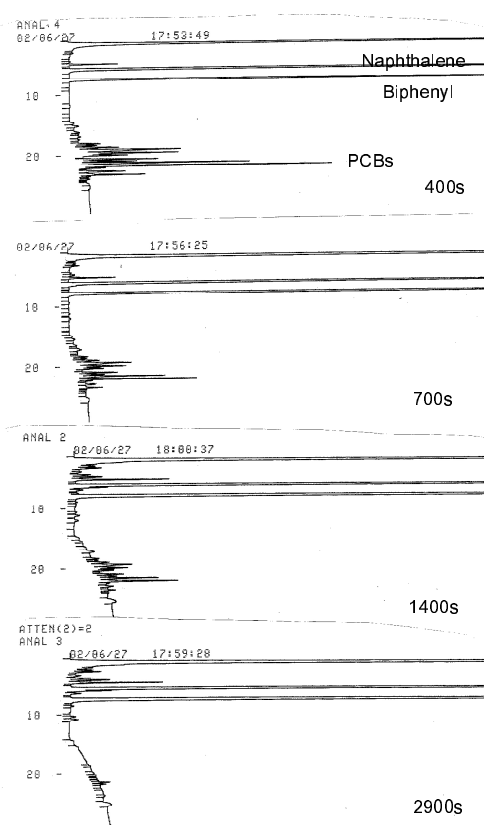


Figure 2. Change of HPLC during electrolysis of Kaneclor 400
Mediator: Naphthalene 5.9 mM
Kaneclor 400: 1.1 mM
Other conditions: The same as in Figure 1