

Catalytic Reduction of 4,4'-(2,2,2-Trichloroethane-1,1-diyl)bis(chlorobenzene) (DDT) with Nickel(I) Salen Electrogenerated at Carbon Cathodes in Dimethylformamide

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In 1939, 4,4'-(2,2,2-trichloroethane-1,1-diyl)bis(chlorobenzene) (DDT) was introduced as a pesticide; within only a few years, it became the most widely used insecticide in the world. By the mid 1970s, however, the Stockholm Convention prohibited the use of this compound throughout the United States due to the discovery that DDT and its degradation products have adverse effects on human health and the environment.^{1,2} Although its global use is severely restricted, DDT is still persistent in the environment, and a strategy for its effective remediation is needed. Research that focuses on the catalytic electrochemical dechlorination of DDT and its reduction products is therefore of interest. In previous work in our laboratory, the direct and cobalt(I) salen-catalyzed reduction of DDT was investigated; it has been determined that 4,4'-(ethene-1,1-diyl)bis(chlorobenzene) (DDNU) and 4,4'-(2-chloroethene-1,1-diyl)bis(chlorobenzene) (DDMU) are the principal products.^{2,3} Up to the present time, no work has been conducted that deals with nickel(I) salen-catalyzed reduction of DDT. Unlike cobalt(II) salen, nickel(II) salen is not air-sensitive, so it can be utilized to effect the reduction under simpler experimental conditions.

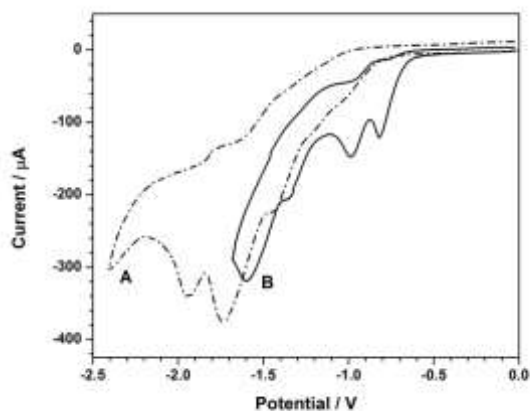


Figure 1. Cyclic voltammograms recorded at 100 mV s^{-1} with a glassy carbon cathode (area = 0.077 cm^2) in DMF containing 0.050 M TMABF_4 and (A) 5.0 mM DDT or (B) $2.0 \text{ mM nickel(II) salen}$ and 5.0 mM DDT .

Preliminary cyclic voltammetric investigations have focused on a comparison of the direct reduction of DDT (Figure 1, curve A) with the catalytic reduction of the same substrate by electrogenerated nickel(I) salen (Figure 1, curve B) in DMF containing 0.050 M TMABF_4 . Curve A shows that DDT undergoes a sequence of five reductions—two shoulder peaks at -1.00 and -1.21 V and three well defined peaks at -1.43 , -1.73 and -1.94 V . In the presence of nickel(II) salen, a significant positive potential shift is observed and only four cathodic peaks are recorded at -0.82 , -0.98 , -1.34 , and -1.60 V .

To further probe the behavior of DDT in the presence of nickel(I) salen, cyclic voltammetry was employed to observe the catalytic reduction of various concentrations of DDT. Shown in Figure 2 are cyclic voltammograms recorded at 100 mV s^{-1} with a glassy carbon electrode for the reduction of $2.0 \text{ mM nickel(II) salen}$ in DMF– 0.050 M TMABF_4 alone (A) and in the presence of (B) 2.0 , (C) 5.0 , (D) 10.0 , and (E) 20.0 mM DDT . Curve B exhibits a prepeak at -0.77 V followed by the reduction peak for nickel(II) salen. As the substrate concentration increases from curve B to E, the prepeak increases in size and shifts toward more negative potentials; the anodic peak for oxidation of nickel(I) salen is severely attenuated at higher concentrations.

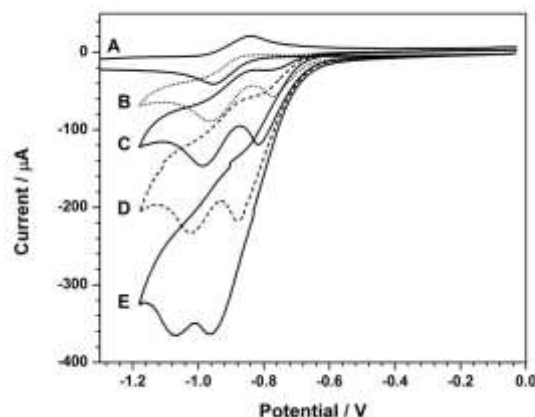


Figure 2. Cyclic voltammograms for $2.0 \text{ mM nickel(II) salen}$ in the presence of (A) 0 , (B) 2.0 , (C) 5.0 , (D) 10.0 , and (E) 20.0 mM DDT recorded at 100 mV s^{-1} with a glassy carbon cathode (area = 0.077 cm^2) in DMF– 0.050 M TMABF_4 .

In addition to cyclic voltammetry, bulk electrolysis, gas chromatography (GC), and gas chromatography–mass spectrometry (GC–MS) have been employed to study the reduction of nickel(II) salen in the presence of DDT. It has been determined that DDNU and 1-chloro-4-styrylbenzene are the major products. For initial DDT concentrations higher than 10 mM , DDMU becomes a more prominent product.

References

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3. Mubarak, M.S.; Gach, P.C.; Peters, D.G. *Electroanalysis* **2006**, *18*, 417–422.
4. Gach, P.C.; Mubarak, M.S.; Karty, J.A.; Peters, D.G. *J. Electrochem. Soc.* **2007**, *154*, F1–F6.
5. All potentials are cited with respect to a reference electrode of saturated cadmium amalgam in contact with DMF, which has a potential of -0.76 V vs. SCE .