# Catalytic Dechlorination of Organochlorine Compounds. I. DDT

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The dechlorination of organochlorine pesticides represents a possible method for their disposal. Up to 62 percent of the organically-bound chlorine is rapidly lost from 2,2-bis-(p-chlorophenyl)-1,1,1-trichloroethane, DDT, in methanol by the catalytic action of nickel boride, $Ni_2B$, with an excess of sodium borohydride, $NaBH_4$. The products of the reaction were determined by gas chromatography/mass spectrometry. Figure 1 shows the sequence of reactions leading to the dechlorinated compounds.

Nickel boride, a black solid, was prepared in situ by the reaction of sodium borohydride with an alcoholic solution of nickel chloride.

$$9\ H_2O + 2\ NiCl_2 + 4\ NaBH_4 \longrightarrow Ni_2B + 12.5\ H_2 + 4\ NaCl + 3H_3BO_3$$

Nickel boride has previously been used for the catalytic hydrogenation of olefins (BROWN and BROWN, 1963; BROWN, 1970; RUSSELL and HOY, 1971). This material also catalyzes the hydrolysis of the borohydride ion to produce hydrogen and borate ion (SCHLESINGER et al., 1953). This is the first time nickel boride has been used as a catalyst for dechlorination, although Raney nickel (KAMMERER et al., 1953; BUU-HOI et al., 1963) and palladium on charcoal (MOSBY, 1959; VINOPAL, et al., 1973) are known to catalyze the removal of chlorine from various chloro-aromatic compounds.

## METHODS

Gas chromatographic analysis of product mixtures was carried out using 1/8" OD by 8 foot, 10% OV-1 on 100/120 mesh GAS CHROM Q, column at 220°C. The structural identification of product components from the reactions were determined by a DuPont 490-B gas chromatograph/mass spectrometer.

The amount of chloride ion produced in the dechlorination of DDT in various systems was determined by titration of an aliquot of the diluted reaction mixture with standard silver nitrate solution using an Orion chloride electrode and reference electrode connected to a Fisher Titrator. A plot of millivolts against the

Bulletin of Environmental Contamination & Toxicology,
Vol. 14, No. 6 © 1975 by Springer-Verlag New York Inc.

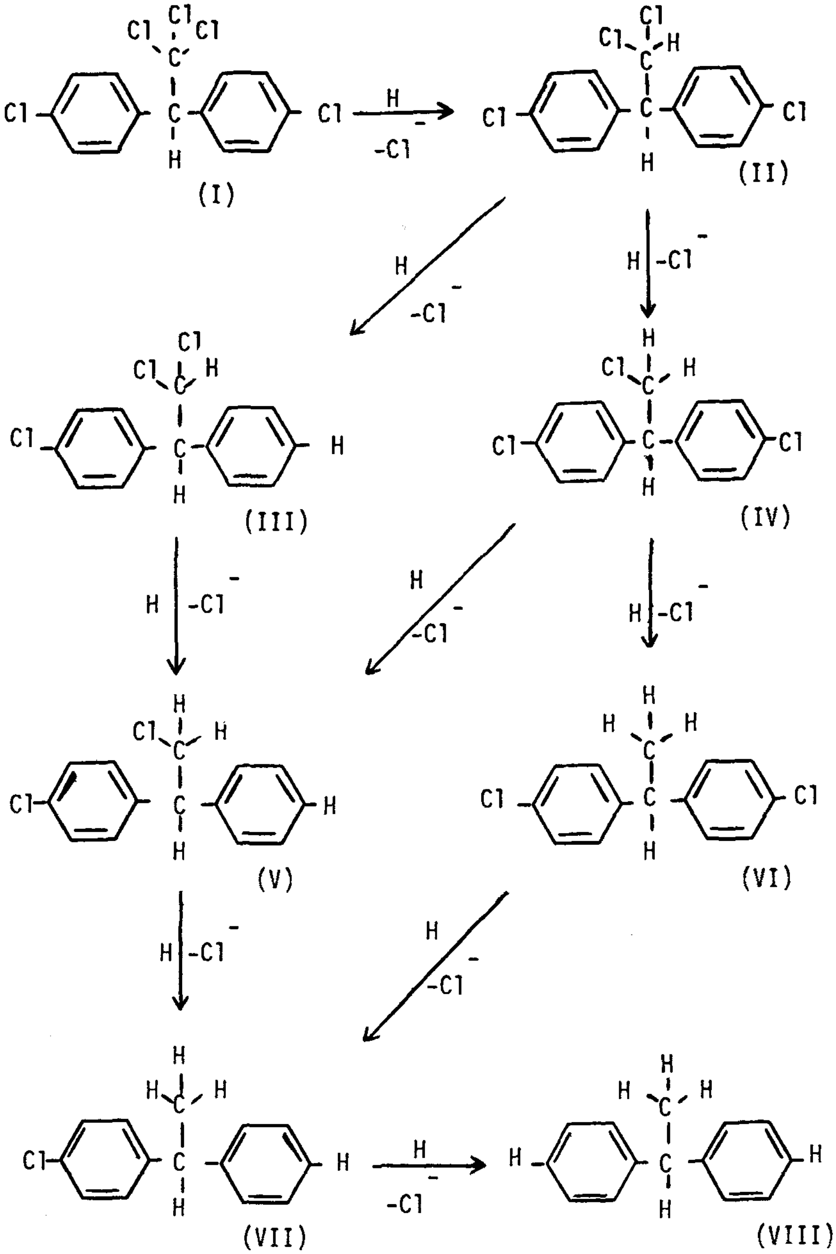

Figure 1. Reaction products and probable sequence for the dechlorination of DDT.

volume of added silver nitrate gives a sine curve with the inflection point as the end point of the titration. Correction was made for the endogenous chloride present due to the nickel chloride.

To dechlorinate DDT, 1 millimole (mmol) of DDT was dissolved in 30 ml of methanol, ethanol or 2-propanol. To this solution was added 0.5 mmol of nickel chloride hydrate (0.25 ml of a 2 M aqueous solution) and the solution stirred until homogeneous. Between 5 and 30 mmol of $NaBH_4$ was added dropwise as a 5 M aqueous solution. The nickel boride formed during the addition of the first few drops of sodium borohydride. Throughout the reaction, hydrogen was evolved from the hydrolysis of the excess borohydride. After a 30 minute reaction time, 100 ml of distilled water was added to the reaction mixture and the organic products extracted into 50 ml of benzene: hexane (1:1, v:v). The aqueous portion of the mixture following extraction was titrated for chloride ion. The organic extract was analyzed by gas chromatography/mass spectrometry. The solvents and reagent concentrations were varied to determine their effects on the efficiency of dechlorination.

## RESULTS AND DISCUSSION

DDT was best dechlorinated in methanol at a 1:15:0.5 mole ratio of DDT:$NaBH_4$:Ni(II). Further addition of sodium borohydride did not significantly increase the extent of dechlorination. This is due in part to the increasing amount of water added to the system from the addition of aqueous sodium borohydride. In fact, it was shown that increasing concentrations of water in a reaction mixture resulted in lower yields of inorganic chloride.

Table 1 shows the chloride production from reactions carried out in different solvents and varying amounts of sodium borohydride. It should be noted that when no $NiCl_2$ is used, 1 mmol of chloride is formed. This comes from the dehydrohalogenation of DDT to 2,2-bis-(p-chlorophenyl)-1,1-dichloroethylene, DDE. This is due to the high alkalinity of the sodium borohydride solution. Table 1 shows that for any given concentration of sodium borohydride, the extent of dechlorination follows the sequence methanol>ethanol>2-propanol.

It is shown in Table 2 that a ratio of 0.5:1, mmol $NiCl_2$: mmol DDT results in maximum chloride production. However, even a ratio of 0.01:1 ($NiCl_2$:DDT) resulted in substantial dechlorination.

The rate of loss of the organically-bound chlorine from DDT is rapid as shown by Figure 2. This rate was determined by the rapid addition of 10 mmol of $NaBH_4$ to 1 mmol of DDT in 20 ml of methanol in the presence of 0.25 mmol of $NiCl_2$. Aliquots were quickly removed and titrated for chloride.

## TABLE 1

### Chloride Produced in the Dechlorination of 1 mmol DDT by the $Ni_2B/NaBH_4$ System as a Function of Solvent and $NaBH_4$ Added ($NiCl_2$ was 0.5 mmol)

| Solvent (30 ml) | NaBH (mmol)$^4$ | Chloride produced* (mmol) |
|---|---|---|
| methanol | 15 | 1.00** |
| methanol | 5 | 2.92 |
| | 10 | 3.10 |
| | 15 | 3.16 |
| | 30 | 3.12 |
| ethanol | 5 | 2.31 |
| | 10 | 2.54 |
| | 15 | 2.68 |
| | 30 | 2.47 |
| 2-propanol | 5 | 2.14 |
| | 10 | 2.22 |
| | 15 | 2.19 |
| | 30 | 2.24 |

*Reaction time was 30 minutes.
**No $NiCl_2$ was added; this chloride results from dehydrohalogenation.

## TABLE 2

### The Effect of Catalyst Concentration on the Dechlorination of 1 mmol DDT in Methanol, with 10 mmol of $NaBH_4$

| $NiCl_2$ (mmol) | Chloride produced (mmol)* |
|---|---|
| 0.00 | 1.00 |
| 0.01 | 2.83 |
| 0.05 | 2.88 |
| 0.10 | 2.92 |
| 0.50 | 3.04 |
| 1.00 | 2.74 |

*Reaction time was 30 minutes.

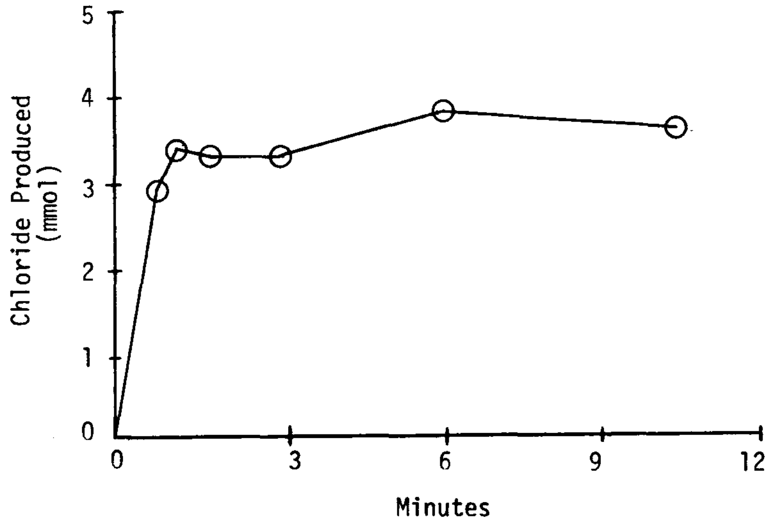

Figure 2. Rate of dechlorination of DDT using the $Ni_2B/NaBH_4$ system in methanol. Conditions: 1 mmol DDT, 20 ml of methanol, 0.25 mmol $NiCl_2$, 10 mmol $NaBH_4$.

The yield of chloride is higher in the reaction shown in Figure 2 than those presented in Table 1 because of the more rapid addition of sodium borohydride in the former case. However, this rapid addition of borohydride results in a violent evolution of hydrogen.

Although DDT can proceed to the completely dechlorinated diphenylethane (VIII), mixtures of this material with the compounds VII, VI, IV, and lesser amounts of V and III, were always obtained. In reactions carried out in methanol with sufficient sodium borohydride and catalyst, no DDT (I) or DDD (II) was found. The inability of DDT to yield only compound VIII is due in part to the sluggishness of reaction of the precursors and to the increasing concentration of water in the system from the addition of the aqueous sodium borohydride.

In order to determine the effect of increasing water concentration in the $Ni_2B/NaBH_2$ system, the dechlorinated products of 1 mmol DDT were isolated by extraction, the solvent evaporated, and the chloride measured. A second dechlorination was then performed on the products and the chloride measured again. Both dechlorinations were carried out in methanol using 15 mmol $NaBH_4$ and 0.5 mmol $NiCl_2$. The initial dechlorination (2 hours) produced 3.71 mmol chloride.

The second dechlorination (30 minutes) gave an additional 0.53 mmol chloride. Thus by sequential dechlorination, it was possible to obtain 4.24 mmol (of a possible 5.00) chloride. It is felt that additional dechlorinations would result in completely dechlorinated DDT.

The reaction of borohydride ion with metal salts is not unique to nickel. A number of other metal borides can be prepared (BROWN and BROWN, 1962). Reactions were carried out with equivalent concentrations of nickel, cobalt, manganese and iron (ferrous) salts, as well as a commercially obtained NiB. The results are summarized in Table 3. The $Ni_2B$ prepared *in situ* produced more chloride than did the other catalysts. The cobalt gave a black precipitable, presumably a boride; whereas, the manganese gave a white solid of unknown composition and no precipitate was formed with the ferrous salt until approximately 30 mmol $NaBH_4$ had been added.

The $Ni_2B/NaBH_4$ system in methanol offers a simple and rapid method to partially dechlorinate DDT. However, the value of this reaction as a disposal method would depend upon the assessment of the biodegradability and toxicity of the reaction products, and its applicability to DDT formulations.

TABLE 3

Comparison of the Catalytic Activity of Various Metal Salts (0.5 mmol) in the Presence of 20 mmol $NaBH_4$ in the Dechlorination of 1 mmol DDT in Methanol.

| Metal Salt | Chloride Produced (mmol) |
|---|---|
| $NiCl_2$ | 3.12 |
| $CoCl_2$ | 2.48 |
| $MnSO_4$ | 2.48 |
| $FeSO_4$ | 0.31 |
| NiB* | 2.49 |

*Commercially available from Ventron Corporation, Alfa Products, Beverly, Massachusetts.

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