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Catalytic Dechlorination of Organochlorine Compounds
V. Polychlorinated Biphenyls—Aroclor 1254

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Polychlorinated biphenyls, PCBs, are pervasive and persistent compounds. Although microbial action is effective in degrading the mono-, di- and trichlorinated biphenyls, it is not effective for biphenyls of higher chlorine substitution (AHMED & FOCHT 1973, FURUKAWA & MATSUMURA 1976). In contrast to the resistance of PCBs to microbial degradation, chemical degradation offers a more effective means for their disposal.

BERG *et al.* (1972) reported the catalytic dechlorination of PCBs at 180°C to biphenyl with 5% platinum or palladium on 60/80 mesh glass beads. More recently, LAPIERRE (1977) showed complete dechlorination of AROCLOR 1248 with 69% nickel on kieselguhr in the presence of sodium hydroxide and 50 atm of hydrogen at 115°C for 6 hrs. Our studies indicated that successful dechlorination of chlorobenzene could be achieved with excess sodium borohydride in the presence of nickel boride in alcohols at ambient temperature and pressure (DENNIS & COOPER 1977). We therefore expected, and have now found, that PCBs would also be amenable to dechlorination by this technique.

METHODS AND MATERIALS

The PCB mixture used was AROCLOR 1254, which contains an average of five chlorine atoms per biphenyl molecule. AROCLOR 1254 and its products of dechlorination were analyzed by GLC. A gas chromatograph equipped with a 1.8m x 2 mm ID glass column containing 3% OV-1 on 80/100 mesh Gas Chrom Q and with a flame ionization detector was used. A gas chromatograph/mass spectrometer provided identification of the dechlorination products.

The process variables examined were the type of solvent and the nickel boride and sodium borohydride concentrations. The volume of solvent, PCB concentrations, and reaction time were held constant.

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AROCLOR 1254, 0.1 g (3×10^{-4} mol), dissolved in 2.3 *ml* of tetrahydrofuran, was added to 50 *ml* of methanol, ethanol, or 2-propanol. To this solution was added an aliquot of 2 *M* $NiCl_2 \cdot 6 H_2O$ in methanol. The resulting solution was then stirred vigorously while an aliquot of 5 *M* aqueous $NaBH_4$ was added dropwise. After 30 min, 200 *ml* of distilled water was added to the reaction mixture. This mixture was then extracted into 50 *ml* of ethyl ether. The ether layer was dried with Na_2SO_4, filtered, then concentrated by evaporation. This concentrate was analyzed by both GLC and GLC/MS.

RESULTS AND DISCUSSION

The most effective dechlorination was achieved in 2-propanol with 2.0 mmol $NiCl_2$, 60 mmol $NaBH_4$ and 0.3 mmol AROCLOR 1254. Biphenyl constituted 97% of the reaction products, and monochloro- and dichlorobiphenyl the remaining products. Biphenyl was confirmed as the main product of dechlorination through comparison with an authentic sample of biphenyl by GLC analysis and GLC/MS. Figure 1 shows the difference between the unreacted AROCLOR 1254 and its products of reaction formed after 30 min in 2-propanol in the presence of Ni_2B and $NaBH_4$.

Where the greatest amounts of nickel chloride and sodium borohydride were used, dechlorination of PCBs in ethanol or methanol was less efficient than in 2-propanol. As the proportions of nickel chloride and sodium borohydride were decreased, the degree of dechlorination in ethanol became negligible, whereas dechlorination of PCBs in methanol showed little change. In experiments where lower ratios of nickel chloride and sodium borohydride to PCBs were used, dechlorination in methanol proved to be more effective than in either ethanol or 2-propanol under similar conditions. Table 1 presents the data for the dechlorination of ARCLOR 1254 in 2-propanol, ethanol and methanol. The percentages of biphenyl, monochlorobiphenyl and dichlorobiphenyl shown in this table were the percent areas from the gas chromatograms. Products of higher chlorine substitution were present in experiments where the biphenyl, monochloro- and dichlorobiphenyl did not add up to 100%.

In summary, the rapid and complete dechlorination of PCBs by sodium borohydride catalyzed by nickel boride in 2-propanol can be conducted at ambient temperature and pressure. The disadvantage of this method is that a rather large ratio of sodium borohydride to PCBs is required to reach complete dechlorination.

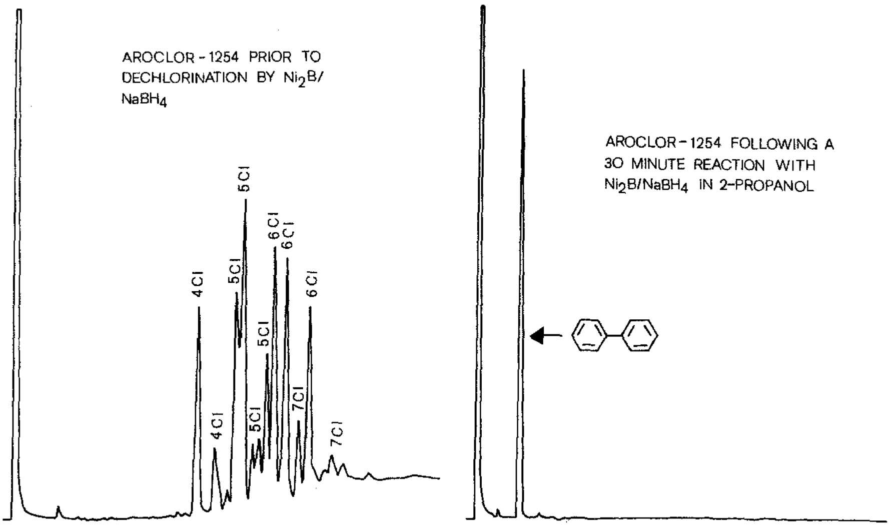

Figure 1. AROCLOR 1254 (0.3 mmol) before and after dechlorination by $NiCl_2$ (2.0 mmol) and $NaBH_4$ (60.0 mmol) in 50 *ml* of 2-propanol.
GLC conditions: In experimental, programmed from 150°C to 250°C at 16/min. and N_2 carrier gas.

TABLE 1

Results of a 30 Min Reaction of 0.1 g AROCLOR in 50 *ml* of Solvent

Solvent	$NiCl_2$ mmol	$NaBH_4$ mmol	% biphenyl	% monochlorobiphenyl	% dichlorobiphenyl
2-Propanol	0.5	15	*	-	-
"	0.5	30	71	10	7
"	2.0	60	97	1	0.1
Ethanol	0.5	15	*	-	-
"	0.5	30	*	-	-
"	2.0	60	85	6	4
Methanol	0.2	60	21	7	22
"	0.5	15	64	6	4
"	0.5	30	75	6	4
"	0.5	45	61	12	19
"	0.5	60	81	4	1
"	1.0	60	79	2	1
"	2.0	60	80	2	0.5

*Negligible dechlorination

REFERENCES

AHMED, M. and D.D. FOCHT: Can. J. Microbiol. 19, 47 (1973).

BERG, O.W., P.L. DROSODY and G.A.V. PEES: Bull. Environ. Contam Toxicol, 7, 338 (1972).

DENNIS, Jr. W.H. and W.J. COOPER: US Army Medical Bioengineering Research and Development Laboratory, Technical Report 7702, AD# A040118, Fort Detrick, MD, April 1977.

FURUKAWA, K. and F. MATSUMURA: J. Agr. Food Chem. 24, 251 (1966).

LAPIERRE, R.B.: EPA Report No. 60013-77-018, Jan 1977.