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The Hydrodechlorination of Chloroaromatic and Unsaturated Chloroaliphatic Compounds Using a Nickel Boride Reagent

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A nickel boride reagent, prepared *in situ* by the reaction of nickel chloride with sodium borohydride, has been used to hydrodechlorinate and hydrogenate chloroaromatic compounds. The same reagent can also dechlorinate chloro-olefinic compounds but chloroalkanes do not react. The reactions can be sustained by addition of hydrogen gas and the ratio of the aromatic to aliphatic hydrocarbons produced can be varied by addition of sodium hydroxide to the reaction mixture and by the duration of the reaction. The reactivity of polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), chlorobenzene and tetrachloroethylene have been studied. Capillary gas chromatography was used to follow the course of reactions and gas chromatography–mass spectroscopy (GC–MS) was used for product identification.

Keywords: hydrodechlorination; nickel boride; chloroaromatic compounds; tetrachloroethylene

INTRODUCTION

Polychlorinated biphenyls (PCBs) and related substances such as polychlorinated naphthalenes (PCNs) and polychlorinated terphenyls (PCTs) are environmentally persistent chemicals which bioaccumulate in fatty tissue and may hence cause damage to wildlife. Although PCBs were introduced into industrial use as early as 1929, the first evidence of their presence in the environment was not observed until the mid-1960s.[1] These chloroaromatic compounds are chemically very stable, with stability increasing with increasing numbers of chlorine atoms attached to the carbon skeleton. Mono- and di-chlorobiphenyls have half-lives of approximately six days for photodegradation in sunlight[2] but higher congeners are far more resistant to attack. Hence they are considered to be the most abundant chlorinated aromatic pollutants in the global ecosystem.[3] Although production of PCBs was ceased officially in the late 1970s, existing materials containing PCBs continue to enter the environment via waste disposal to landfill and inefficient incineration processes.

Toxicology of PCBs, and to a lesser extent PCNs, has been associated with chloracne, skin discloration, liver dysfunction and reproductive defects (especially in fish-eating birds) and they may be co-carcinogens in humans. Impurities (dioxins and furans) in PCBs further complicate the issue of toxicity.

Because of their toxicology and persistence in the environment, disposal of chloroatomic compounds is not a simple process. Typically, high-temperature incineration is used with temperatures in excess of 1100 °C being necessary to prevent dioxin and furan formation during the incineration process.

Catalysed low-temperature hydrodechlorination was first proposed by Thompson *et al.*,[4] who used palladium on alumina with hydrogen at 200 °C to hydrodechlorinate various organochlorine compounds. This reaction was simplified by Beroza,[5] who mounted the catalyst in the injection port of a gas chromatograph, used hydrogen as both a carrier gas and a reagent gas, and effectively reduced the process to one of on-column derivatization. This technique was subsequently developed by Cooke and Roberts for quantization of PCBs in environmental samples,[6] for use with capillary gas chromatography,[7] and for the detection of chlorinated aliphatic compounds in complex mixtures.[8]

An alternative method for hydrodechlorination derives from the work of Brown and Brown,[9] who used a nickel boride catalyst and hydrogen gas to hydrogenate olefins. Dennis and Cooper[10] modi-

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fied the reaction to achieve at least partial dechlorination of some organochlorine pesticides, including DDT (technical grade). The nickel catalyst was prepared *in situ* by reaction of sodium borohydride with nickel chloride; it has the empirical formula $(Ni_2B)_2H_3$. It is black and amorphous. Subsequently Kozlinski[11] reported its use for the dechlorination of PCBs.

Although it shows considerable promise as a hydrodechlorination catalyst, the use of nickel boride and borides of other transitional metals has centred primarily on hydrogenation and this chemistry has been extensively reviewed.[12] Recently the versatility of nickel boride has been demonstrated by its use as a desulphurization catalyst for benzo- and dibenzo-thiophenes.[13] Best results were obtained with *in situ* generation of nickel boride. The proposed mechanism required complexation of the substrate on the nickel boride surface followed by stepwise reduction of the two carbon–sulphur bonds. Hydrodechlorination has also been achieved using palladium on carbon in the presence of formic acid and water[14] to reductively dechlorinate chlorinated aromatic compounds. We now report the use of nickel boride both to hydrodechlorinate and to hydrogenate not only chloroaromatic linked-ring compounds such as PCBs, but also fused-ring systems such as PCNs, single-ring compounds such as chlorobenzene, and even the chlorinated unsaturated aliphatic compound, tetrachloroethylene.

EXPERIMENTAL

Chemicals

Solvents, hexadecane and undecane (internal standards), chlorobenzene, tetrachloroethylene and dichloromethane were obtained from BDH (Poole, Dorset, UK), as was nickel chloride (AnalaR) and sodium borohydride. PCBs (Aroclors) were donated by Monsanto (Newport, Gwent, UK) and PCNs (Nibren waxes) were supplied by Bayer (Leverkusen, Germany). Alcohol solvents were used as received but hexane was redistilled before use.

Equipment

Capillary gas chromatography was performed on a Carlo Erba Series 2451 gas chromatograph equipped with a split/splitless injector and flame ionization detector. Data were acquired by chart recorder (Servoscribe 1s, 10 mV fsd) and by recording integrator (Hewlett–Packard Model 3392, 1 V input). The fused silica column was coated with SP2100 (a non-polar methylsilicone, 12 m × 0.18 mm i.d., df = 0.25 μm). The carrier gas was hydrogen ($1.5\ \mathrm{ml\ min^{-1}}$), the injection port temperature 250 °C and the detector temperature 280 °C. A typical temperature programme was 60 °C, hold 1 min, then $6\ ^\circ\mathrm{C\ min^{-1}}$ to 200 °C, then $10\ ^\circ\mathrm{C\ min^{-1}}$ to 250 °C, hold 5 min, then cool. Mass spectrometry was performed either on a VG Micromass 16F or a Hewlett–Packard MSD instrument, and was used to confirm peak identity only.

Reaction procedure—large scale

The alcohol or chosen alcohol mixture (30 ml), 0.25 ml of 2 M nickel chloride solution and 2 ml of a solution in alcohol of a chlorinated compound (10-fold excess over nickel chloride) were stirred in a 50-ml beaker at room temperature using a Teflon-coated magnetic stirring bar. To the stirred solution was added 5 ml of sodium borohydride solution (5 M). Nickel boride was immediately generated as a finely divided black powder.

Periodically 1-ml aliquots of the reaction mixture were withdrawn from the beaker and added to a test-tube containing distilled water (5 ml) and hexane (1 ml) containing the internal standard (IS) (undecane or hexadecane), thus quenching the reaction. The tube was shaken vigorously to partition the organic compounds from the reaction into the hexane layer, which was removed and dried over anhydrous sodium sulphate. A 1 μl aliquot was chromatographed and the relative amounts of the various products were assessed by ratioing peak areas against that of the internal standard. Ratios were plotted against time (see Fig. 1 for an example) to show the appearance of various products during the reaction. Variables in this scheme were the nature of the alcohol solvent, the type of chlorinated compound and the nickel boride/chlorocarbon ratio.

Reaction procedure—small scale

The large-scale procedure was subsequently varied as follows. A test-tube (150 mm × 20 mm) replaced the beaker. A water bath surrounded the test-tube to control the reaction temperature. A fritted bubbler was immersed in the reaction mixture to provide additional hydrogen gas if desired.

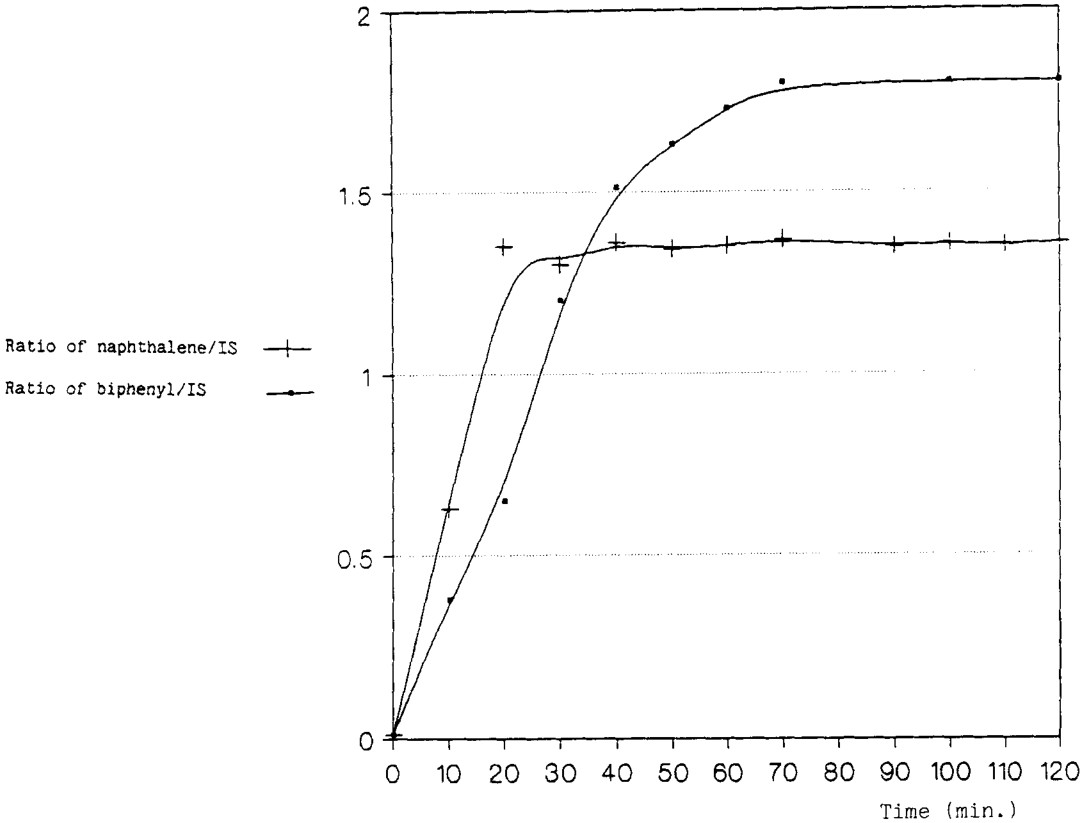

Figure 1 Comparison of the relative concentrations of naphthalene (○) and biphenyl (●) from Aroclor 1248 and Nibren wax D88 by hydrodechlorination with nickel boride/sodium borohydride.

RESULTS AND DISCUSSION

Hydrodechlorination of PCB and PCN compounds

Using the large-scale reaction procedure, aliquots of PCB (Aroclor 1248) and PCN (Nibren wax D88) were treated with nickel boride/sodium borohydride in isopropanol. Samples were removed periodically over 2 h. After gas-chromatographic analysis, the ratios of the areas of naphthalene/IS and biphenyl/IS were plotted against time to give the results shown in Fig. 1. Reaction of PCN is rapid, being some 50% complete after *ca* 10 min. PCB reaction is slower, being 50% complete after *ca* 25 min and essentially complete after 70 min. The decrease in the rate of formation of biphenyl towards the end of the reaction suggests that some PCB congeners were difficult to dechlorinate fully whereas the PCN proceeded smoothly to completion.

To evaluate the efficiency and reproducibility of the reaction it was repeated ten times and the resultant naphthalene and biphenyl calculated as a percentage of the theoretical yield. The PCB and PCN materials used were assumed to be pure. For naphthalene the average yield was 86.4% (standard deviation 5.45%). For biphenyl the average yield was 52.8% (standard deviation 8.82%). If the contribution from bicyclohexane (resulting from dechlorination and hydrogenation) is included, the average yield rises to 89.0% of the theoretical yield for biphenyl.

In order to reduce the consumption of sodium borohydride, the possibility of generating the nickel boride with a small quantity of sodium borohydride and then sustaining the reaction by bubbling hydrogen gas through the reaction mixture was investigated. The small-scale reaction procedure was used, with Aroclor 1248 only being reacted in sufficient quantity to ensure that some residual Aroclor 1248 remained when effervescence ceased after some 40 min of reaction. The reaction was then stirred for 10 min and a sample was removed and analysed (Fig. 2A). At this point some PCB remained in the reaction mixture

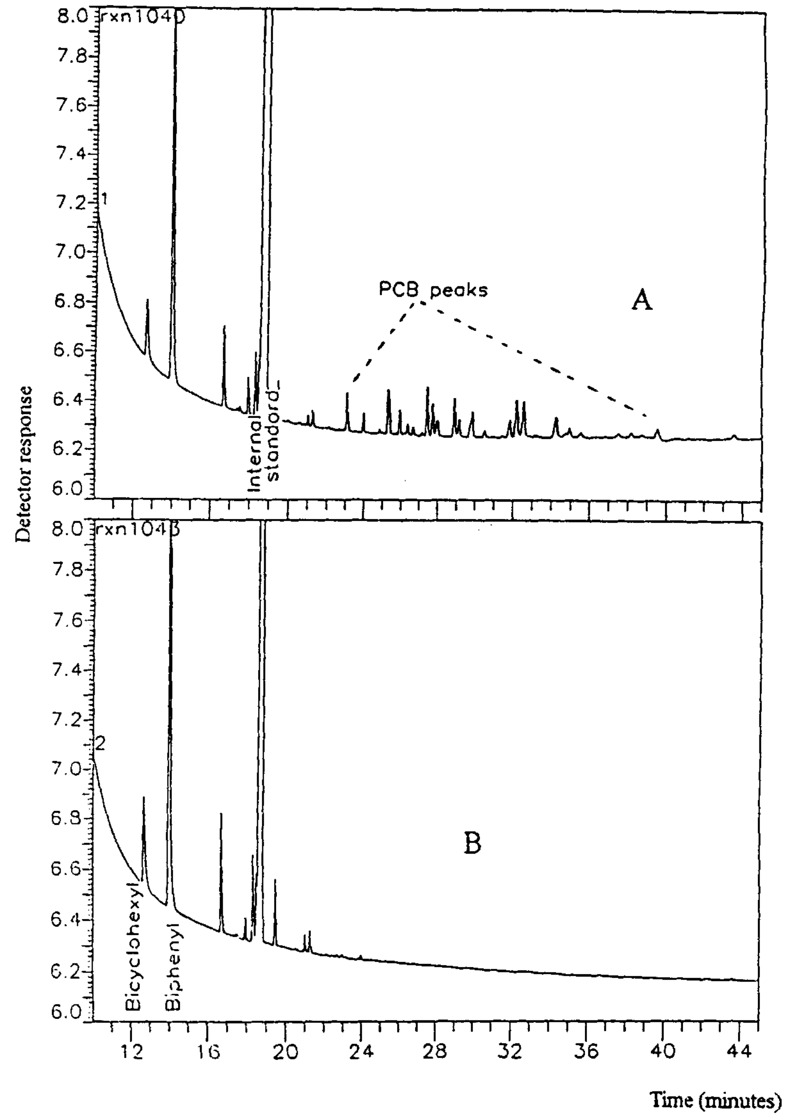

Figure 2 (A) Distribution of residual chlorinated compounds from Aroclor 1248 after reaction with nickel boride/sodium borohydride until exhaustion of the sodium borohydride was observed. (B) The same reaction mixture after bubbling hydrogen gas for a further 60 min.

but the sodium borohydride was exhausted. Hydrogen was then bubbled through the reaction mixture for *ca* 60 min and a second sample taken (Fig. 2B). In Fig. 2(A) both bicyclohexyl (retention time of component, $t_R = 12.6$ min) and biphenyl ($t_R = 14.0$ min) are present, as are a range of chlorobiphenyls ($t_R = 21$–39 min). A chlorine atom content of 1–4 per molecule was indicated by mass spectrometry. In Fig. 2(B) bicyclohexyl and biphenyl were again present, as were a group of hydrocarbon impurities clustered around the internal standard. These were present in both Figs 2(A) and 2(B), however. The addition of hydrogen gas thus appears to sustain the reactivity of the nickel boride, allowing the reaction to proceed further. The possibility of loss of PCB by adsorption onto nickel boride was considered but rejected because of the presence of alcohol as a solvent. Alcohols are strongly polar solvents and, as such, are often used as desorbing solvents.

As hydrochloric acid is formed in the reaction it must be lost either by evaporation, or more likely, by reaction to form sodium chloride. The effect of adding sodium hydroxide to the reaction mixture was therefore investigated. Two small-scale reactions on Aroclor 1248 were performed in parallel with one reaction mixture containing 5 ml of 0.25 M sodium hydroxide solution. Hydrogen gas was bubbled through both reaction mixtures. Aliquots were removed periodically over 6 h. The reaction without sodium hydroxide produced biphenyl in excess of bicyclohexyl in the early stages but after 4 h the concentrations were approximately equal and after 6 h the ratio was *ca* 60% bicyclohexyl to 40% biphenyl. In contrast, the reaction mixture containing sodium hydroxide proceeded more quickly, with the biphenyl concentration matching that of bicyclohexyl after only 2 h. Thereafter the biphenyl content decreased and the bicyclohexyl content increased, with the final ratio being approximately 8:92 (Fig. 3). The chromatograms for the samples taken after 2 h are shown in Fig. 4. Clearly the dechlorination proceeds more rapidly in the presence of sodium hydroxide. Some other conclusions can be drawn. Dechlorination is approaching completion after 2 h, thus confirming the previous results of a combined PCB and PCN sample. The presence of hydrogen gas appears to promote the formation of bicyclohexyl in competition with biphenyl but hydrogenation of biphenyl to bicyclohexyl as a secondary reaction proceeds only slowly, if at all. However, the presence of sodium hydroxide in addition to hydrogen gas appears to promote the hydrogenation of biphenyl, as the bicyclohexyl concentration rises as that of biphenyl declines. Previously only partial hydrogenation of polycyclic aromatic hydrocarbons has been reported.[15]

Hydrodechlorination of other chloro compounds

Chlorobenzene (20 ml, 0.001 M) was reacted with 0.15 ml of 2 M nickel(II) chloride ($NiCl_2$) solution and 1.75 ml of 5 M sodium borohydride solution using the small-scale procedure with hydrogen gas. After 10 min 1.7% of the original amount of chlorobenzene was left. After 20 min dechlorination was complete (no detectable chlorobenzene in the reaction mixture). The dechlorination product was benzene; hexane was therefore considered to be an unsuitable solvent for partitioning of products as it would obscure the benzene peak when chromatographed. Carbon disulphide was used instead of hexane and the chromatographic conditions adjusted accordingly.

Similarly, tetrachloroethylene (TCE, 20 μl) was reacted using the small-scale procedure but without hydrogen gas to avoid loss of TCE by evaporation. The reaction vessel was jacketed with ice water and lightly stoppered to minimize evaporative loss due to the evolution of hydrogen gas from the borohydride. Hexane was used as the extracting solvent and the temperature programme was modified (by increasing the ramp rate to 25 °C min^{-1}) to provide a rapid analysis. After reaction for 20 min the evolution of hydrogen ceased and a sample of the reaction mixture was removed and chromatographed. Comparison of the peak area ratios for TCE against the internal standard indicated that approximately 70% of the TCE had been removed, with ethylene being the probable end-product. For this experiment the TCE concentration was 0.01 M (cf. 0.001 M for chlorobenzene) which, together with the lower reaction temperature, may explain why only partial dechlorination had occurred after 20 min.

Similarly dichloromethane (0.10 M) was reacted with freshly prepared nickel boride/sodium borohydride in isopropanol but, after 30 min, no observable dechlorination had occurred.

A series of experiments were performed to evaluate the activity of nickel boride and its sustainability. Nickel boride was freshly prepared, filtered off, dried and stored for several days. It was then used in a dechlorination reaction with sodium borohydride but reactivity was found to be poor. Addition of hydrogen gas produced little improvement. Freshly prepared nickel boride stored in alcohol and not isolated retains its activity for some time but it slowly declines. Maintenance under hydrogen gas sustains reactivity for much longer. It would appear that reactivity is associated with a combination of nickel boride and hydrogen and that if this reactive hydrogen is lost from the nickel boride it is difficult to replace.

CONCLUSIONS

The nickel boride/sodium borohydride in isopropanol reaction system is capable fo hydrodechlorination of linked-ring (PCB) and fused-ring (PCN) chlorinated aromatic compounds. It can also dechlorinate monoaromatic chloro compounds such as chlorobenzene and chlorinated alkenes such as tetrachloroethylene. However, saturated species such as dichloromethane and polychlorinated alkanes based on a C_{14}–C_{17} hy-

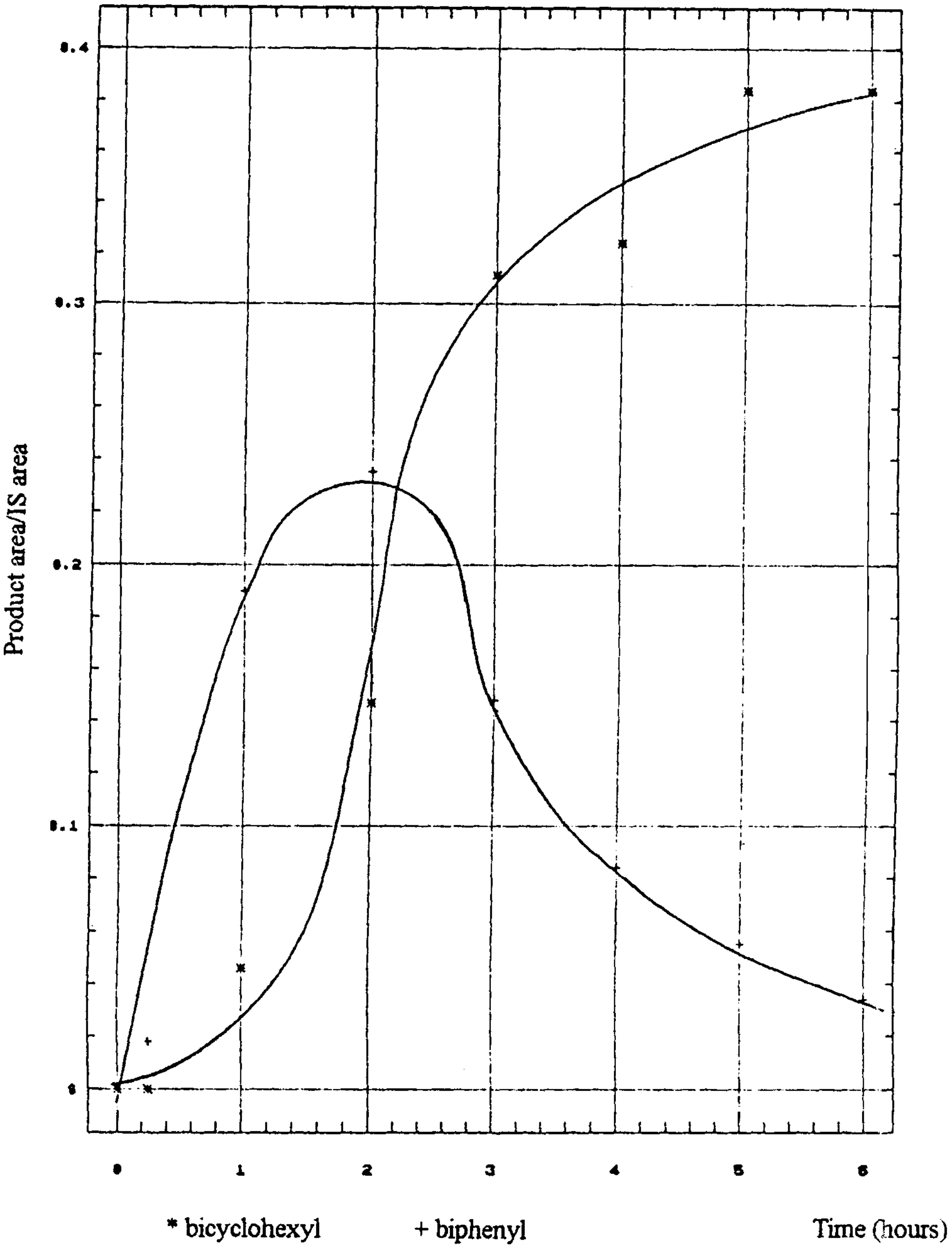

Figure 3 Relative concentrations of biphenyl and bicyclohexyl formed from Aroclor 1248 in the presence of sodium hydroxide and hydrogen gas.

drocarbon fraction (M. Cooke and D. J. Roberts, unpublished observations) do not react. Hence a degree of unsaturation appears to be necessary for the reaction to proceed. This is in contrast with the behaviour of chloroalkanes when passed over heated metal catalyst in a hydrogen atmosphere.[16] Hydrogen gas appears to be capable of sustaining the reaction once it is initiated, and hence the reaction shows promise for the disposal of unsaturated waste chlorinated compounds. Brominated aromatics also react (M. Cooke and D. J. Roberts, unpublished observations). Nickel boride should be prepared and used *in situ* as attempts to prepare, isolate and store the reagent ready for subsequent use, in our hands, produced a catalyst with low reactivity.

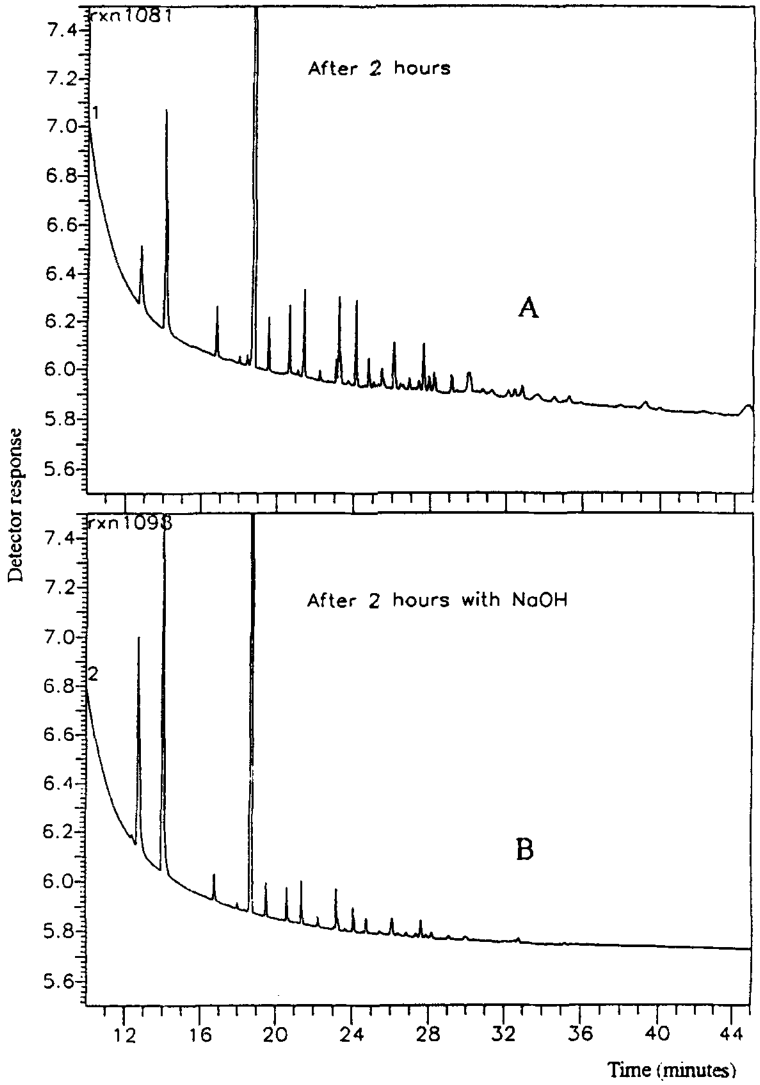

Figure 4 Comparison of the profiles of the reaction products formed by hydrodechlorination of Aroclor 1248 after 2 h without (A) and with (B) addition of sodium hydroxide.

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