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APPLICATIONS OF AMMONIUM FORMATE CATALYTIC TRANSFER HYDROGENOLYSIS--IV[1]:

A FACILE METHOD FOR DEHALOGENATION OF AROMATIC CHLOROCARBONS

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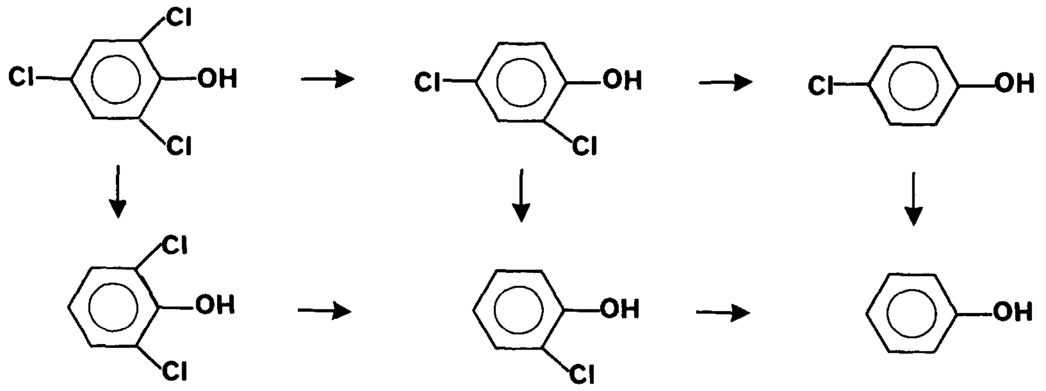
ABSTRACT: Ammonium formate catalytic transfer hydrogenolysis, in the presence of palladium on carbon, has shown utility for the rapid dehalogenation of mono-or polychlorinated aromatic compounds in neutral media under ambient conditions of temperature and pressure.

The facile removal of halogen from aryl halides is of both preparative[2] and environmental significance.[3] Dehalogenation at high temperatures followed by pyrolysis is one of the preferred approaches in the detoxification of pollutants such as PCBs, dioxins, and other chloroaromatics. We now wish to report a safe, efficient, and energy conservative system with which complete dehalogenation of a standard PCB mixture, Aroclor 1254, was achieved in less than 4 minutes, in a batch reaction mode. We have previously described a rapid transfer hydrogenolytic procedure, utilizing ammonium formate as the hydrogen donor, for deprotection of benzyl esters and benzyl ethers,[4] for reductive cleavage of N-guanidyl-nitro groups,[4] and for quantitative removal of organic macromolecules bound to insoluble polymer supports via a benzyl ester link.[1,5] The ambient temperature and pressure conditions utilized in ammonium formate-catalytic transfer hydrogenation (AF-CTH), even with difficult transformations,[1,4,5,6] provided the impetus for applying this system to the problem of polyhalogenated pollutants.

Initially AF-CTH was applied to the dehalogenation of m-chlorobenzoic acid in the presence of one fourth its weight of 10% Pd-C and an excess of ammonium formate. Reversed phase-high performance liquid chromatographic (RP-HPLC) analysis showed the reaction to be complete in under 10 minutes (Figure 1).

To assess the scope of AF-CTH and to determine probable regioselectivity in the dehalogenation of polychlorinated compounds, 2,4,6-trichlorophenol was selected as the next model substrate. This compound is of particular interest due to its structural similarity to 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), a potent herbicide, defoliant, and an active ingredient of "agent orange." Also, the symmetrical nature of 2,4,6-trichlorophenol would permit easy detection of regioselectivity due to a decreased number of isomeric species that could result, if the reductive cleavage were to proceed in a serial manner (Scheme 1).

Scheme 1



RP-HPLC scrutiny of the dehalogenation reaction of 2,4,6-trichlorophenol (Table 1) led to the following conclusions: (1) Presence of only trace amounts of p-chlorophenol throughout the course of reaction are indicative of the regioselective vulnerability of the chlorine attached at the para position; (2) by comparing several reactions under different conditions, it was observed that 10% Pd-C was a much better catalyst than 1% Pd-C on an exact metal content basis, suggesting that the density of population of palladium atoms in a supported catalyst may be critical for its efficacy[7]; (3) with higher catalyst concentrations, as in a continuous flow reaction, AF-CTH should find practical application in the detoxification of polychlorinated compounds. This was substantiated by the complete dehalogenation of 2,4,6-trichlorophenol achieved by passing a methanolic solution of substrate and ammonium formate through a column of 10% Pd-C admixed with a small amount of silica gel. The time required for column through-put (<1 minute) proved to be adequate.

TABLE 1. Product Analysis of Dehalogenation of 2,4,6-trichlorophenol by RP-HPLC

REACTION TIME (MIN)	% PHENOL	% 2-CHLORO-PHENOL	% 2,6-DICHLORO-PHENOL	% 2,4-DICHLORO-PHENOL	% 2,4,6-TRI-CHLOROPHENOL
1	49.1	4.8	5.1	15.4	25.7
5	96.1	1.3	0	1.9	0.7
10	100	0	0	0	0

Reaction conditions: 2,4,6-trichlorophenol (1.0 g), 10% Pd-C (0.5 g), methanol (10 ml), saturated aqueous ammonium formate (2 ml)

The facility of AF-CTH for these dechlorination reactions suggests that it could be the reagent of choice for rapid dehalogenation of environmentally undesired species such as 2,4,5-T and polychlorinated biphenyls (PCB's). Accordingly, a standard commercial PCB mixture of Aroclor 1254 was subjected to AF-CTH (Equation 1) as outlined in the experimental section.

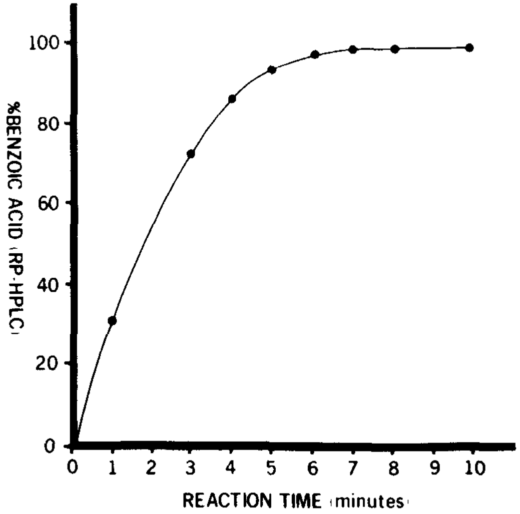


FIGURE 1.

Reaction parameters: m-chlorobenzoic acid (1.0 g), 10% Pd-C (0.25 g), water (2 ml), methanol (16 ml), saturated aqueous ammonium formate (ca. 2 ml).

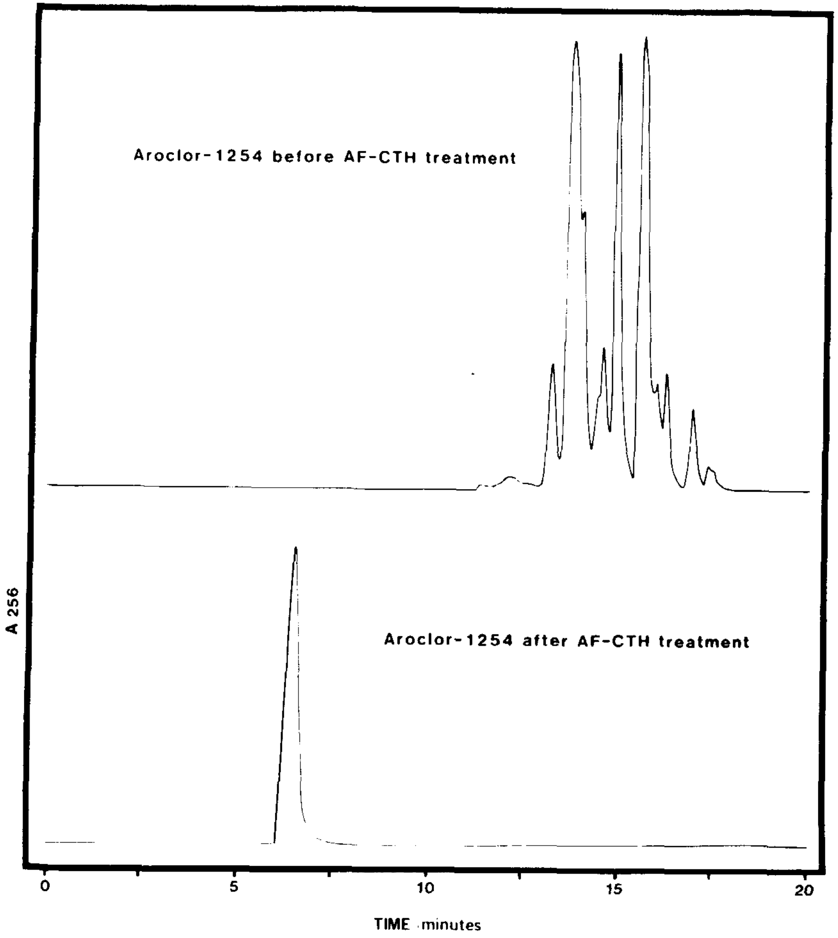
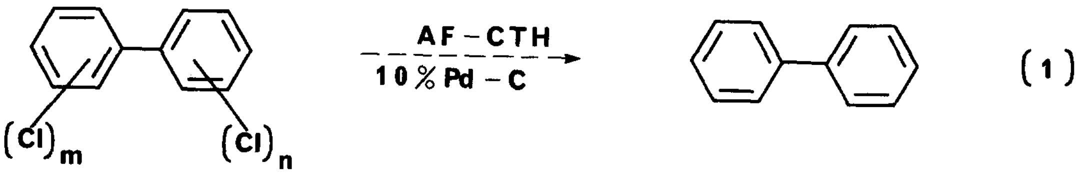


FIGURE 2. RP-HPLC profiles of Aroclor 1254 before and after AF-CTH treatment:



In this case, no attempt was made to detect the intermediates for lack of suitable standards. The reaction time for complete dehalogenation was assessed by RP-HPLC and was found to be less than 4 minutes (Figure 2). A detailed kinetic analysis of the reaction course of 2,4,6-trichlorophenol dehalogenation (outlined in Scheme 1) as well as applications of AF-CTH (in both batch and continuous flow modes) to other organic and environmentally important compounds will be reported at a later date.

EXPERIMENTAL

General procedure for dehalogenation of aryl halides using AF-CTH: To a solution of the aryl halide and ammonium formate (4 to 5 molar equivalents) in methanol or aqueous acetic acid, the catalyst, 10% palladium-on-carbon (1/4 to 1x the weight of aryl halide) was added. The addition of catalyst is best done under an oxygen free atmosphere. Reaction aliquots after filtration through a plug of glass wool and celite, were analysed by RP-HPLC. After the completion of reaction, the catalyst was removed by filtration and the filtrate concentrated under reduced pressure. The product was isolated either by precipitation with water or by extraction into a suitable organic solvent such as ethyl acetate or chloroform.

AF-CTH of a Standard PCB mixture: Aroclor 1254: To a solution of Aroclor 1254 (0.44 g) in tetrahydrofuran (2 ml), methanol (48 ml), and ammonium formate (3 g) were added and stirred until homogenous. Next, 10% Pd-C (0.44 g) was added under a nitrogen atmosphere, at which point rapid effervescence was observed. RP-HPLC analysis of an aliquot of the reaction mixture taken at 4 minutes indicated the reaction to be 100% complete, and the sole product of the reaction to be biphenyl (Fig. 2). Filtration of the catalyst, followed by evaporation of solvents and addition of water yielded biphenyl (0.20 g), identical in all respects to an authentic sample.

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