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ENHANCED PHOTODEHALOGENATION OF CHLOROBIPHENYLS

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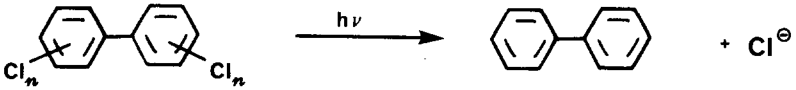
Summary: The rate of photodechlorination of chlorobiphenyls in acetonitrile/water is dramatically enhanced when the compounds are irradiated in the presence of sodium borohydride. This rate enhancement is even larger in micellar solutions.

Pollution by aromatic halides such as polychlorobiphenyls has led to increasing attention to photolysis as a method for their destruction.[1] However, improved rates and efficiency of photodehalogenation are necessary if photolytic processes are to be generally practical. An early study by Barltrop[2] reported a free radical chain mechanism for the photodechlorination of benzene when sodium borohydride was present. However, the reported quantum yield (0.5) was not significantly greater than that for "simple" photodechlorination in the absence of sodium borohydride,[3] which is about 0.4 to 0.5. Later, Tsujimoto[4] reported labeling experiments involving 3- and 4-chlorobiphenyl which suggested that they did not dechlorinate by a free radical chain mechanism when irradiated in the presence of sodium borohydride. Since neither of these studies performed parallel experiments comparing the presence and absence of sodium borohydride, it was not apparent whether an actual rate enhancement was observed in either case. We have performed such experiments with some environmentally-important chlorobiphenyls, and observed universally that a dramatic enhancement of their rate of photodechlorination occurs when sodium borohydride is present.



Photolysis of the chlorobiphenyls in 9:1 acetonitrile:water with an Osram HNS 10 W/U OFR low pressure mercury lamp led cleanly to dechlorination products. However, the addition of sodium borohydride significantly increased the rate of the reaction (See Figure 1 and Table 1) while giving the same overall reaction.[5]

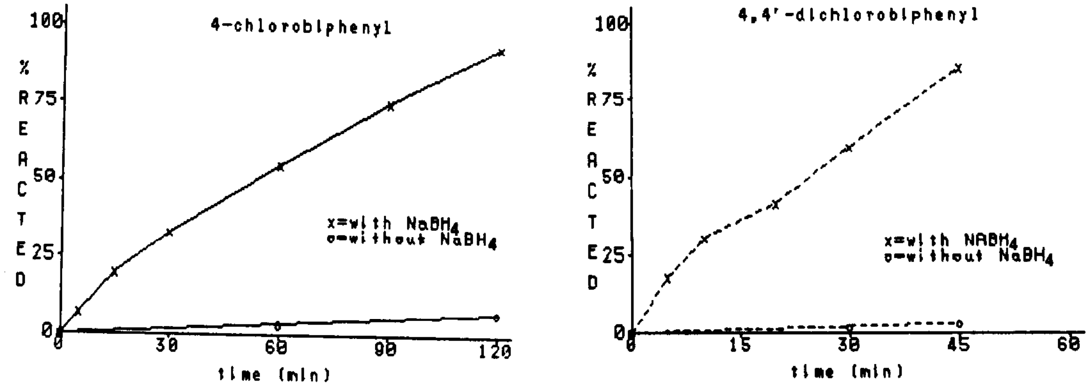


Figure 1. Photodestruction of 4-chloro- and 4,4'-dichlorobiphenyl in the presence and absence of sodium borohydride.

Table 1. Quantum Efficiency for Photodechlorination of Chlorobiphenyls in 9:1 Acetonitrile/water.

	Φ With $NaBH_4$	Φ Without $NaBH_4$	Ratio
3-chloro-	0.082	0.0051	16.
4-chloro-	0.013	0.00090	14.
4,4'-dichloro-	0.050	0.0010	50.
2,2',5,5'-tetrachloro-	0.14	0.025	5.6

With all compounds a significant increase in the rate of photodestruction (and quantum yield for photolysis) was observed. The increase was particularly significant with the more photostable isomers, where traditional photodestruction is less effective. The products of photolysis when sodium borohydride was present continued to be the simpler dechlorinated compounds. The chlorine that was lost was transformed into chloride ion, which was detected using a chloride selective ion electrode, calibrated with authentic mixtures of known concentration.

With chlorobenzene Barltrop reported that the photodehalogenation in the presence of sodium borohydride was via a free radical chain reaction, because the reaction could be completely inhibited by the presence of small amounts of acrylonitrile (a scavenger for the free radical intermediates). In contrast, we find that the sodium borohydride-enhanced photodehalogenation of 4-chlorobiphenyl was unaffected by acrylonitrile, even at a 10-fold excess in comparison with 4-chlorobiphenyl. Similarly, irradiation in the presence of other radical scavengers (butylhydroxytoluene, hydroquinone, and oxygen) failed to affect the quantum yield of the borohydride-enhanced photodechlorination. Consequently, in accord with the conclusions of Tsujimoto[4] from his deuterium-labeling studies, we conclude that the dechlorination does not proceed via a free radical chain mechanism. A mechanism involving a direct attack of hydride on the photoexcited biphenyls is consistent with the experimental results, because a non-chain mechanism involving borohydride after the normal photochemical fission of chlorine would not increase the quantum efficiency.

Because the solubility of polychlorinated biphenyls in polar solvents is low,[6] we have explored experimental modifications which could react higher concentrations of these less soluble materials than would be possible in ordinary solutions. In this regard, micellar solutions were examined, since in these solutions the PCB's would have considerably higher solubility[6] than in acetonitrile/water. Under these conditions, using aqueous solutions of sodium borohydride, sodium dioctyl sulfosuccinate (0.06 M), and 4-chlorobiphenyl, we found an even greater enhancement of the dechlorination efficiency, with the quantum yield increasing to 0.030, a 33-fold enhancement of the quantum efficiency in comparison with photolysis in solution without sodium borohydride. We further examined the effect of radical scavengers on the enhanced photolysis in micelles, and observed no decrease in the efficiency of the dehalogenation when scavengers were present. Thus, it does not appear that a free radical chain mechanism is operable in micelles. Rather, it appears that the enhancement is a medium effect[7] with the biphenyl residing in the hydrocarbon interior, and being attacked by borohydride that is either at the interface or penetrating slightly into the hydrocarbon region.

Since the borohydride enhancement of the efficiency of photodechlorination of the chlorobiphenyls appears to be a general phenomenon, we are continuing to explore the versatility of this reaction with similar, complex chloroaromatic compounds.

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5. Typically photolyzing 50-100 mg of biphenyls in 75 ml of 9:1 acetonitrile/water that contained 0.5 g of sodium borohydride. Photoproducts were isolated by extraction for comparison of their spectra with those of authentic compounds. Quantitation was performed using HPLC, using an IBM octadecyl column (4.5 x 250 mm), eluting at 1 ml/min with a mobile phase of 70:30 acetonitrile/water. Typical retention times under these conditions were: biphenyl, 9.5 min; 4-chlorobiphenyl, 12.5 min; 4,4'-dichlorobiphenyl, 16.5 min. Quantum yields were determined using benzophenone/benzpinacol actinometry, using disappearance of starting materials at low conversion.

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