

Borohydride-enhanced Dechlorination of Chlorobenzenes and Toluenes

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Photolysis of chlorobenzenes and chlorotoluenes in the presence of sodium borohydride leads to a faster photochemical reaction, with enhancements of rate of up to a 100-fold. The photoproduct mixtures become less complex in the presence of sodium borohydride, predominantly forming the dechlorinated aromatic hydrocarbon in near-quantitative yield. In some cases, though not all, a chain mechanism appears operative.

The photoreactivity of aryl chlorides has been intensively studied,¹ and photochemical dechlorination has generally been observed in a great variety of compounds. This reaction is important both because it is intrinsically interesting and because the photodechlorination is of potential value as a method of detoxification of aryl chlorides which are important environmental pollutants.² However, two major shortcomings limit the practicality of photodechlorination as a detoxification path: low quantum yields and side reactions. Polychlorinated biphenyls (PCB's), for example, have quantum yields of dechlorination as low as 0.0003.³ The quantum yield is typically low in those compounds lacking an *ortho* chlorine but bearing *meta* or *para* substituents.⁴ Unfortunately, these are frequently the more toxic isomers.⁵ Side reactions in the photolysis of chlorobenzenes commonly involve formation of chlorophenols and chlorobiphenyls,⁶ while photolysis of PCB's give rise to a variety of products, including the more toxic chlorinated dibenzofurans.⁷ Hence, modification of the 'normal' photo-reaction paths of chloroaromatic compounds in a manner that overcomes these deficiencies would potentially be of practical value.

In a preliminary communication Barltrop⁸ observed that the quantum yield of photoreaction of bromobenzene and iodobenzene was substantially increased when sodium borohydride was present during photolysis. Unfortunately, for chlorobenzene the observed quantum yield (0.5) was close to the values reported in the absence of sodium borohydride,⁹ suggesting little enhancement of photolysis rate, if any. Our observation¹⁰ of dramatic increases in the quantum yield of dechlorination of chlorotoluenes led us to a comprehensive study of the family of chlorobenzenes and some representative chlorotoluenes. This study has shown the borohydride enhancement of photolysis rate to be general, and leads to cleaner photoreaction to give the dechlorinated aromatic compounds.

Experimental

Materials.—Chlorobenzenes and chlorotoluenes were obtained from Aldrich Chemical Co., except for pentachlorobenzene, which was from Lancaster Synthesis. Samples were generally of satisfactory purity as received; exceptions were distilled or vacuum distilled prior to use. Acrylonitrile (Aldrich) was freshly distilled prior to use. Sodium borohydride was obtained from Fisher Scientific. Other materials (scavengers and quenchers) were obtained from Aldrich and used as received.

Irradiations.—Solutions of *ca.* 0.02M of the halide in 9:1 acetonitrile–water were prepared using Baker 'Photrex' acetonitrile and deionized water that was further purified using a cartridge purification system. Irradiations used an Osram HNS W/U OFR mercury lamp, an Applied Photophysics

model RS-50 Semi-Micro Photochemical Reactor, or a Rayonet RPR-100 Chamber Reactor, equipped with RPR-2537 lamps. Benzophenone/benzpinacol actinometry was used to establish the light output of the lamps. Irradiations in the presence of sodium borohydride typically contained from 0.2M to 0.4M sodium borohydride.

Quantification.—The extent of photolysis was quantified by h.p.l.c. or g.c. H.p.l.c. analysis utilized an IBM Ternary Gradient HPLC equipped with an octadecyl-bonded silica column, 4.5 × 250 mm. Typically, 7:3 acetonitrile–water was used as the eluant. Gas chromatography used a Perkin-Elmer Sigma 4 chromatograph equipped with thermistor detectors and an OV-1 column. In some cases quantification used a Hewlett-Packard chromatograph equipped with a cross-linked methyl silicone gum column (12 m × 0.2 mm). This chromatograph was connected to a model 5970B Mass Spectrometer, allowing g.c./m.s. analysis of photolysis mixtures. In each case, the average of duplicate or triplicate injections was used in the calculation of the percent reaction.

Products.—Products were determined by isolation (column chromatography) followed by n.m.r. analysis of the isolated materials, or by g.c./m.s. analysis, the retention times and mass spectra being compared with those of authentic materials.

Results and Discussion

Enhancement of Photodechlorination by Borohydride.—The photodechlorination of chlorobenzene has been well studied, and a wide range of values for quantum yield of photoreaction reported. Some reported values are: 0.52^{9a} (in cyclohexane), 0.38^{9b} (cyclohexane), 0.25¹¹ (cyclohexane), 0.13¹² (methanol), 0.10^{6a} (water), and 0.012^{9b} (Freon). These disparate values seem to reflect differences in solvent, methodology, and the type of actinometer used. Even greater differences are found in reported quantum yields for other chlorobenzenes. For example, 1,4-dichlorobenzene was reported to react with quantum yields of 0.17,¹¹ 0.10,^{6a} 0.040,¹² 0.0045,¹³ and 0.0040.¹⁴ Consequently, it was clear that an accurate appraisal of the effect of borohydride on the photoreaction of chlorobenzenes would require the parallel determination of the rate of reaction both in the presence and in the absence of borohydride (in the same solvent and at the same concentration of halide). In this way an enhancement of rate would be clearly evident, obviating the necessity of choosing the 'best' or 'most appropriate' value from the disparate reports which are available. Thus, we examined all of the chlorobenzenes in the presence and absence of sodium borohydride; the results are summarized in Table 1.

It is apparent from Table 1 that the photoreaction of all of the chlorobenzenes is enhanced by the presence of borohydride. The enhanced rate of destruction was shown to be a true

Table 1. Sodium borohydride-enhanced dechlorination of chlorobenzenes (comparative quantum yields of disappearance)

| Compound | ϕ_r With borohydride ^a | ϕ_r Without borohydride | Enhancement ratio |
|---|--|------------------------------|-------------------|
| Chlorobenzene | 2.14 | 0.40 | 5.4 |
| 1,2-Cl ₂ C ₆ H ₄ | 0.40 | 0.080 | 5.1 |
| 1,3-Cl ₂ C ₆ H ₄ | 0.21 | 0.056 | 3.8 |
| 1,4-Cl ₂ C ₆ H ₄ | 0.51 | 0.050 | 10 |
| 1,2,3-Cl ₃ C ₆ H ₃ | 0.38 | 0.093 | 4.1 |
| 1,2,4-Cl ₃ C ₆ H ₃ | 0.29 | 0.035 | 8.3 |
| 1,3,5-Cl ₃ C ₆ H ₃ | 0.27 | 0.029 | 9.4 |
| 1,2,3,4-Cl ₄ C ₆ H ₂ | 0.38 | 0.083 | 4.6 |
| 1,2,3,5-Cl ₄ C ₆ H ₂ | 0.27 | 0.049 | 5.5 |
| 1,2,4,5-Cl ₄ C ₆ H ₂ | 0.50 | 0.040 | 12 |
| | 0.93 ^b | 0.072 ^b | 13 ^b |
| 1,2,3,4,5-Cl ₅ C ₆ H | 0.27 | 0.039 | 6.9 |
| | 0.85 ^b | 0.094 ^b | 9.0 ^b |
| 1,2,3,4,5,6-Cl ₆ C ₆ ^b | 0.67 | 0.28 | 2.4 |

^a 0.18M. ^b In AOT micelles.**Table 2.** Sodium borohydride-enhanced dechlorination of chloro toluenes (comparative quantum yields of disappearance)

| Toluene | ϕ_r With borohydride ^a | ϕ_r Without borohydride | Enhancement ratio |
|---------------------|--|------------------------------|-------------------|
| 2-Cl | 0.23 | 0.044 | 5.2 |
| 3-Cl | 0.21 | 0.022 | 9.6 |
| 4-Cl | 0.34 | 0.0037 | 92 |
| 2,6-Cl ₂ | 0.42 ^b | 0.11 | 3.8 |
| 2,5-Cl ₂ | 0.79 ^b | 0.025 | 32 |

^a 0.45M. ^b 0.18M.

photochemical process by incubating the chlorobenzenes in the dark with sodium borohydride, and confirming that under these conditions no reaction occurred.

In our preliminary study we reported the photoreaction of chlorotoluenes was enhanced by borohydride. The reaction of more highly chlorinated toluenes appears similarly enhanced (Table 2).

Thus, for any substitution pattern and any amount of chlorination, the presence of borohydride enhances the rate of photoreaction of the chlorobenzenes. For those compounds which ordinarily undergo the most sluggish photoreaction the enhancement is the most pronounced, but in all cases some level of enhancement is observed.

Products of Borohydride-enhanced Photodechlorination.—Normally, photoreaction of chlorobenzenes (like other chloroaromatic compounds) gives rise to a variety of products such as the reduced aromatic compound, phenols, and biphenyls. The second concern addressed above concerning photodestruction of chloroaromatic compounds was the tendency to form materials (such as chlorobiphenyls) which were even more toxic than the starting compound. Accordingly, we have addressed the determination of the products of photoreaction in the presence of borohydride for comparison with those observed in the absence. In all cases we have found the presence of borohydride to cause a 'cleaner' photoreaction in that photoreduction proceeds without simultaneous formation of phenols and higher oligomers. Two representative examples show typical results (Tables 3 and 4).

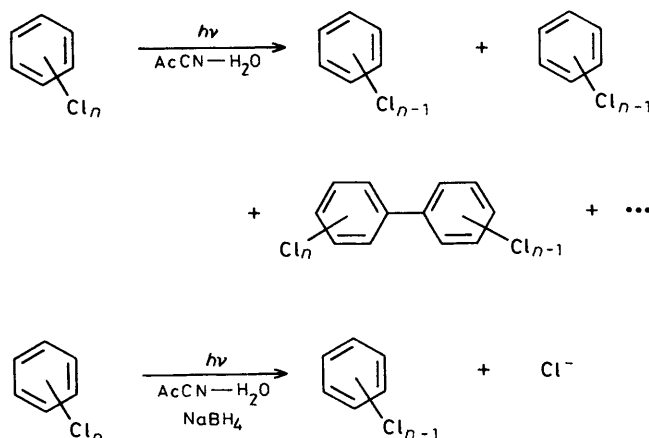
The borohydride-assisted photolysis led to quantitative formation of photoreduction products, even at high conversions, whereas the ordinary photolysis led to a host of products, with 'simple' photoreduction often being less predominant than 'side

Table 3. Products (%) from 1,3-dichlorobenzene^a photolysis

| Compound | Without borohydride ^b | With borohydride ^c |
|---------------------|----------------------------------|-------------------------------|
| Benzene | 0 | 4 |
| Chlorobenzene | 48 | 94 |
| 1,2-Dichlorobenzene | 6 | 2 |
| Dichlorobiphenyls | 8 | 0 |
| Trichlorobiphenyls | 38 | 0 |
| Other | 0 | 0 |

^a 0.018M in acetonitrile-water (9:1). ^b At 10% conversion. ^c At 27% conversion.**Table 4.** Products (%) from 1,2,4-trichlorobenzene^a photolysis

| Compound | Without borohydride ^b | With borohydride ^c |
|---|----------------------------------|-------------------------------|
| C ₆ H ₅ | | 1 |
| ClC ₆ H ₅ | 0 | 18 |
| 1,2-Cl ₂ C ₆ H ₄ | 0.3 | 2 |
| 1,3-Cl ₂ C ₆ H ₄ | 6 | 43 |
| 1,4-Cl ₂ C ₆ H ₄ | 79 | 37 |
| Other | 14 | 0 |

^a 0.018M in acetonitrile-water (9:1). ^b At 12% conversion. ^c At 50% conversion.

reactions'. Of particular importance is the observation of 38% trichlorobiphenyls from 1,3-dichlorobenzene.

Effect of Concentration on Borohydride-assisted Photolyses.—The concentration of two species is of potential concern in the assisted photolysis—the borohydride concentration, and the concentration of the chloroaromatic. The effect of borohydride concentration was addressed first; the results with 4-chlorotoluene as a substrate are shown in Figure 1.

The Figure shows an initial sharp increase in the rate of photoreduction with increase in borohydride concentration, reaching a peak at *ca.* 0.6M, and then declining slightly. At this value we observed a 'salting-out' effect whereby the borohydride caused the 90% acetonitrile/water to become two phases. The largely aqueous phase would contain a higher concentration of borohydride, while the largely acetonitrile phase would contain the greatest concentration of the chloroaromatic compound. Thus, phase separation leads to less enhancement by borohydride than when the solution remains homogeneous. To ensure reliable measurements, most of our work was performed at concentrations lower than the 'optimum', typically at 0.18M.

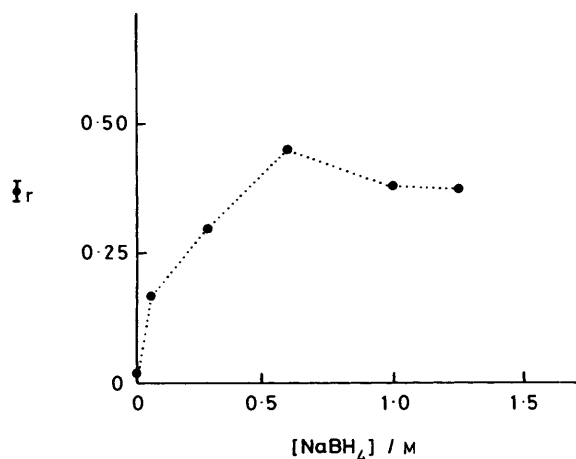


Figure. Effect of borohydride concentration on 4-chlorotoluene photoreduction

Thus, greater borohydride enhancements are probably possible than are shown in the above data, but even at 0.18M the reactions are 'clean' and significant enhancements observed. Barltrop's study⁸ used '1.0M' sodium borohydride in 6% aqueous acetonitrile. In our hands this consistently separated into two phases, which would account for some of the differences between his data and the present study.

The second important variable is the concentration of the chloroaromatic compound. Chlorobenzene showed a significant effect of varying concentration. Table 5 shows the change of quantum yield of dechlorination as the concentration of chlorobenzene is varied.

Thus, at high concentrations a great enhancement is observed, which significantly is the only instance in which we have observed a quantum yield exceeding unity for the chloroaromatic compounds. With other chlorobenzenes there was little effect of concentration upon the quantum yield of borohydride-assisted photoreduction. For example with 1,4-dichlorobenzene a quantum yield of 0.48 was measured at 0.054M and a quantum yield of 0.51 measured at 0.018M. Several other compounds similarly failed to show a significant concentration-dependence. Because of their limited solubility it is impossible to prepare highly concentrated solutions of most chloroaromatic compounds—chlorobenzene is an exceptional case.

Solvent Effect of Borohydride Enhancement.—To determine the best solvent for borohydride-assisted photodechlorinations a series of irradiations were performed using 3- or 4-chlorotoluene as the reactant. The results are summarized in Table 6.

In methanol the reaction of the hydride with solvent is rapid unless the temperature is controlled. The values in Table 6 in this solvent reflect a reaction performed between 0 and 5 °C. Experiments at 25 to 35 °C gave lower quantum yields, but work-up of the solution showed the borohydride to have been considerably exhausted by reaction with solvent during photolysis. The highest quantum yields were observed in ethanol–water (9:1), where values were about twice as great as in acetonitrile–water (9:1). Lower values were observed in those compounds in which the solubility of sodium borohydride was lower. Again, for convenience, we standardized on acetonitrile–water (9:1) for the great bulk of our studies, because its better volatility allowed product isolation more conveniently than in ethanol–water. Nevertheless, great enhancements due to borohydride would perhaps have been evident in Table 1 had this solvent been consistently utilized.

Table 5. Effect of chlorobenzene concentration on borohydride-assisted^a photodechlorination

| [Chlorobenzene]/M | φ _r |
|-------------------|----------------|
| 0.45 | 2.14 |
| 0.090 | 0.57 |
| 0.045 | 0.45 |

^a 0.18M Sodium borohydride in acetonitrile–water (9:1).

Table 6. Effect of solvent on borohydride-assisted photodechlorination of chlorotoluenes

| Toluene | Concentration (M) | Solvent ^a | Borohydride | |
|---------|-------------------|----------------------|--------------------|----------------|
| | | | Concentration (M) | φ _r |
| 3-Cl | 0.021 | 90% EtOH | 0.070 | 0.40 |
| 3-Cl | 0.021 | 90% EtOH | 0.035 | 0.40 |
| 3-Cl | 0.021 | MeOH ^b | 0.035 | 0.37 |
| 3-Cl | 0.1 | 90% MeCN | 0.070 | 0.21 |
| 4-Cl | 0.1 | 90% EtOH | 0.070 | 0.88 |
| 4-Cl | 0.1 | 90% MeCN | 0.070 | 0.38 |
| 4-Cl | 0.021 | MeOH ^b | 0.037 | 0.37 |
| 4-Cl | 0.1 | PEG 400 | 0.070 ^c | 0.18 |
| 4-Cl | 0.1 | Bu ^t OH | 0.070 ^c | 0.083 |

^a Remaining percentage is water. ^b At 0 °C. ^c Saturated in borohydride—actual concentration is lower than this value.

Table 7. Effect of other hydrides on enhanced photodechlorination

| Toluene | Hydride | φ _r |
|---------|---------------------------------------|----------------|
| 2-Cl | None | 0.044 |
| 2-Cl | NaBH ₄ | 0.23 |
| 2-Cl | NaBH(OMe) ₃ | 0.12 |
| 3-Cl | None | 0.022 |
| 3-Cl | NaBH ₄ | 0.21 |
| 3-Cl | NaBH ₃ CN | 0.14 |
| 3-Cl | NaBH(OMe) ₃ (100% AcCN) | 0.25 |

Enhancement Using other Hydrides.—Our initial choice of sodium borohydride was principally because of its compatibility with aqueous solutions, its stability, and its low cost. However, other hydrides were subsequently evaluated for comparison. Typical results are shown in Table 7.

The other hydrides also lead to enhancement, but appear to offer no substantial advantages.

Effect of Micelles.—Briefly mentioned above was the low solubility of chloroaromatic compounds in polar solvents. This was a particular problem with the highly chlorinated materials, because their rapid photoreaction in the presence of borohydride made irradiation times extremely short, and prevented irradiation of large quantities of material. Since the solubility is greater in detergent solutions, these solutions were examined in the presence of borohydride, and found to exhibit even greater enhancements of rate. Representative values for such studies are included in Table 1.

Effect of Scavengers and Quenchers.—We were puzzled by the contrast between the effect of scavengers on chlorotoluene photoreduction in our previous study¹⁰ and Barltrop's report that the photoreduction of chlorobenzene was 'totally inhibited by the presence of small amounts of acrylonitrile.'⁸ Despite exhaustive efforts, we were unable to reproduce his observation.

We found the effect of acrylonitrile was only *partial* inhibition of chlorobenzene photoreduction, and with other compounds there was little or no effect. For example, with chlorobenzene (0.45M) in acetonitrile-water (9:1) containing 0.18M sodium borohydride the quantum yield was diminished from 2.1 to 1.4 by the presence of 0.45M acrylonitrile. 1,2-Dichlorobenzene reacted slightly faster in the presence of 0.05M acrylonitrile ($\phi = 0.49$ as compared to 0.40 in its absence). Other compounds were unaffected by acrylonitrile, as described in our previous report.¹⁰ Other radical scavengers (butylhydroxytoluene, dodecanethiol, and oxygen) similarly had little effect on the quantum yield of borohydride-assisted photoreduction. The ϕ for the borohydride-assisted photoreduction of 4-chlorotoluene (0.34) diminished to 0.30 in the presence of 0.1M acrylonitrile, 0.36 in the presence of butylhydroxytoluene, and 0.27 in the presence of hydroquinone. 1,2-Dichlorobenzene diminished from 0.40 to 0.38 in the presence of 0.02M dodecanethiol. The presence of oxygen slightly decreased the quantum yield for borohydride-assisted photoreduction in most cases. 1,2-Dichlorobenzene diminished from 0.40 to 0.28; 1,4-dichlorobenzene diminished from 0.51 to 0.42; 1,2,4-trichlorobenzene diminished from 0.29 to 0.28; and 4-chlorotoluene (0.34) was 0.36 (within experimental error) in the presence of oxygen.

Mechanism of Borohydride-enhanced Dechlorination.—It is apparent from the results cited above that the mechanism of borohydride enhancement is more complex than originally proposed by Barltrop.⁸ A chain mechanism such as postulated by Barltrop is clearly implicated in those cases where the quantum yield exceeds unity, though with the chlorobenzenes and chlorotoluenes this is infrequently observed—essentially only with chlorobenzene itself at very high concentrations. In other cases the failure to attenuate the reaction rate by radical scavengers such as acrylonitrile suggests enhancement by a mechanism not involving a radical chain pathway. Possibilities include a direct attack by hydride on excited chloroaromatic, single electron transfer from borohydride to excited chloroaromatic compound (followed by cleavage of the resulting radical anion), or X-philic attack¹⁵ by hydride on halogen. A path involving single electron transfer from borohydride could also be the initial step of a mechanism which also includes chain propagation. Experiments to more clearly distinguish between these possibilities are currently underway.

It should be noted that the previous report⁸ that acrylonitrile totally inhibits the photoreduction is not consistent with the accompanying proposed mechanism. In the limiting case—totally efficient scavenging of all radicals by acrylonitrile—the observed quantum yield would be the *unenhanced* quantum yield (perhaps about 0.4 for chlorobenzene), because the chain initiation step (which results in a dechlorination) would be unaffected. Radical scavengers will never totally inhibit photoreduction unless acting as excited state quenchers or absorbing the incident light. As indicated above, our observation of *partial* inhibition of the photoreduction of chlorobenzene by acrylonitrile in the presence of borohydride is indeed consistent with Barltrop's proposed mechanism. However, other chlorobenzenes do not exhibit the same behaviour.

Conclusions.—The photoreduction of chlorobenzenes by photolysis in the presence of borohydride does indeed offer two advantages over 'normal' photolysis—a cleaner photoreaction and higher quantum yields. The generality of this observation suggests potential value for selective photoreductions or photodestructions of undesirable toxic materials.

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