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Enhanced Photodehalogenation of Chlorotoluenes

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The rate of photochemical dechlorination of *p*-chlorotoluene in acetonitrile–water solutions is dramatically enhanced by the presence of sodium borohydride, though a radical chain mechanism does not appear to be an important reaction pathway.

Contamination of our environment by aromatic halides has led to increasing attention to photolysis as a method for their destruction.[1] Improved rates and efficiency of photodehalogenation is of importance if photolytic processes are to be practical. Barltrop and Bradbury[2] have reported a high quantum yield for dechlorination of chlorobenzene in the presence of sodium borohydride ($\Phi = 0.5$), by a mechanism that appears to be a chain reaction. However, the reported quantum efficiency was not substantially greater than that for photodechlorination of chlorobenzene in the *absence* of sodium borohydride in other solvents,[3] which is *ca.* 0.4 to 0.5. There was also some doubt that the chain mechanism was general, because Tsujimoto *et al.*[4] found the results of labelling experiments involving chlorobiphenyls to be incompatible with Barltrop's mechanism. Since it was unclear from either study whether any enhancement of the rate of reaction resulted from the presence of sodium borohydride, we have studied the chlorotoluenes as representative models of halogenoaromatic species, and by comparison can now report that their rate of photolysis is dramatically enhanced by the presence of sodium borohydride.

Photolysis of *p*-chlorotoluene in 9 : 1 acetonitrile–water with an Osram HNS W/U OFR lamp led cleanly to toluene. However, the addition of sodium borohydride led to a dramatic enhancement of the rate of the reaction (see Figure 1), while giving the same overall reaction to form toluene.†

The photolysis of the other chlorotoluenes also proceeded much more rapidly when sodium borohydride was present (see Table 1) though the enhancement ratio was not as great as with the more photostable *p*-chlorotoluene.

The mechanism of chlorobenzene photolysis in the presence of sodium borohydride was attributed to a chain mechanism.[2] However, this does not seem to be general. Tsujimoto *et al.*[4] have demonstrated deuterium incorporation into chlorobiphenyl, which is incompatible with this mechanism. We find that the addition of various radical scavengers does not lead to a significant reduction of the rate of the borohydride-enhanced photodechlorination of *p*-chlorotoluene, unlike the report for chlorobenzene.[2] Whereas Barltrop and Bradbury[2] report that the comparable photoreduction of chlorobenzene was 'totally inhibited by the presence of small amounts of acrylonitrile', we find that the quantum yield for *p*-chlorotoluene was 0.30 in the presence of 0.1 M acrylonitrile. Similarly, the quantum yield was diminished only slightly (to 0.27) by hydroquinone, was unaffected by butylhydroxytoluene ($\Phi = 0.36$) or the presence of oxygen ($\Phi = 0.36$), and diminished (to 0.23) by the presence of n-dodecanethiol. Thus, in contrast to Barltrop and Bradbury's 'total quenching' consistent with a radical chain mechanism, we find that such a

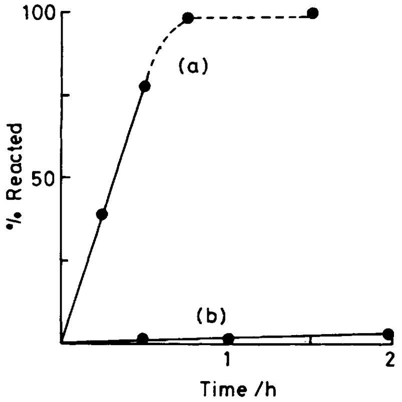

Figure 1. Photodechlorination of *p*-chlorotoluene in acetonitrile–water; (a) in the presence of $NaBH_4$; (b) in the absence of $NaBH_4$.

Table 1. Quantum efficiency for photodechlorination of chlorotoluenes.

Isomer	With $NaBH_4$	Without $NaBH_4$	Ratio
ortho	0.23	0.044	5.2 : 1
meta	0.21	0.022	9.6 : 1
para	0.34	0.0037	92 : 1

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† Typically using 3.5 g of sodium borohydride in 75 ml of acetonitrile–water that was 0.1 M to 0.3 M in *p*-chlorotoluene.

chain mechanism is here at most a small component of the mechanism. Since some exciplex quenching may be involved with the thiol, it is conceivable that the reaction proceeds entirely by a non-chain mechanism. Further, it was apparent that dechlorination in the presence of sodium borohydride showed little dependence on chlorotoluene concentration. A chain mechanism would most likely show a substantial dependence on substrate concentration. Thus, it appears that a path other than a chain reaction, such as direct hydride attack, leads to the observed enhancement of the photolysis rate.

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