CHEMISTRY LETTERS, pp. 963-966, 1990.

# Efficient and Stable Photocatalytic Systems for Reductive Dechlorination of p-Chlorobiphenyl by Sodium Borohydride

Masashi ISHIKAWA[†] and Shunichi FUKUZUMI*
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka 565

Acridine Derivatives (9,10-dihydro-10-methylacridine and acriflavine) act as efficient and stable photocatalysts for reductive dechlorination of p-chlorobiphenyl as well as dehalogention of bromochlorobenzenes with sodium borohydride in acetonitrile/$H_2O$ (9:1 v/v) at 298 K. In the case of acriflavine, the limiting quantum yield at irradiation wavelength $\lambda$ = 350 nm has reached 0.63.

Photochemical reductive dechlorination of chlorinated compounds has recently been studied extensively, in part due to their role as environmental pollutants.[1-7] Although several photocatalytic systems for reductive dechlorination have so far been reported,[3,4] it is desired to develop much more efficient and stable photocatalysts which have sufficient spectral overlap with the solar spectrum.

This study reports efficient and stable photocatalytic systems for reductive dechlorination of p-chlorobiphenyl, which is known to be most difficult to be reduced among PCBs,[7] as well as dehalogenation of bromoclorobenzenes using sodium borohydride ($NaBH_4$) and acridine derivatives as a reductant and photocatalysts, respectively.

No appreciable photoreduction of p-chlorobiphenyl (ClBP) by $NaBH_4$ occurs in the absence of photocatalyst in a mixture of acetonitrile and $H_2O$ ($MeCN/H_2O$, 9:1 v/v) under the irradiation of light from a Xenon lamp as shown in Fig. 1 (part a).[8] When 9,10-dihydro-10-methylacridine ($AcrH_2$) or acriflavine ($AFH^+$) is added to this system at 298 K, each species acts as an efficient photocatalyst for reductive dechlorination of p-chlorobiphenyl with $NaBH_4$ to yield biphenyl as shown in Fig. 1 (part b or c), where the yield of biphenyl was determined by glc. No appreciable photo-

---

[†] Present address: Laboratory of Organic Chemistry, Osaka Women's University, Sakai, Osaka 590.

degradation of the catalysts was observed during the photocatalytic reaction, since the concentration of $AcrH_2$ remained unchanged. When $AcrH_2$ is replaced by the oxidized form, 10-methylacridinium perchlorate ($AcrH^+ClO_4^-$), essentially the same result is obtained, since $AcrH^+$ is immediately reduced by $NaBH_4$ to yield $AcrH_2$ selectively.[9)] Thus, $AcrH_2/AcrH^+$ redox pair acts as an efficient and stable photocatalyst for dechlorination of ClBP with $NaBH_4$. Efficient dehalogenation of o-, m-, p-bromochlorobenzenes also occurs by using the present photocatalytic system.[10)]

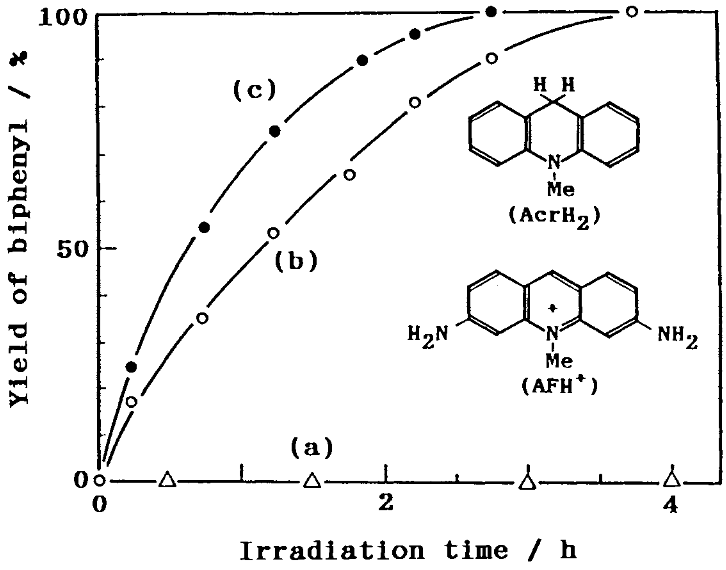


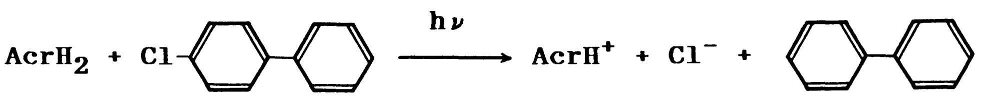
Fig. 1. Photodechlorination of p-chlorobiphenyl (0.10 mol $dm^{-3}$) with $NaBH_4$ (1.0 mol $dm^{-3}$) in $MeCN/H_2O$ (9:1 v/v) (a) in the absence of catalyst ( △ ), (b) in the presence of $AcrH_2$ ($2.0 \times 10^{-2}$ mol $dm^{-3}$) ( ○ ) and (c) $AFH^+$ ($2.0 \times 10^{-2}$ mol $dm^{-3}$) ( ● ) under the irradiation of light from a Xenon lamp. Plots of yield of biphenyl vs. irradiation time.

Since the one-electron oxidation potential ($E^0_{ox}$) of the singlet excited state $^1AcrH_2{}^*$ is known to be largely negative ($E^0_{ox}$ = -3.1 V vs. SCE),[11)] $^1AcrH_2{}^*$ may act as a very strong reductant. In fact, the fluorescence of $^1AcrH_2{}^*$ is readily quenched by ClBP. From the Stern-Volmer plot is obtained the Stern-Volmer constant ($K_{SV}$) as $1.2 \times 10^2$ $dm^3$ $mol^{-1}$. The fluorescence lifetime ($\tau$) of $^1AcrH_2{}^*$ in $MeCN/H_2O$ (9:1 v/v) was determined as 7.0 ns by using the single photon counting technique. Thus, the quenching rate constant ($k_q = K_{SV}\tau^{-1}$) is obtained as $1.7 \times 10^{10}$ $dm^3$ $mol^{-1}$ $s^{-1}$ which is close to the diffusion rate constant.[10)] The $K_{SV}$ value for the fluorescence quenching of the reduced form of acriflavine ($^1AFH_2{}^*$) by ClBP is also obtained as $3.6 \times 10^1$ $dm^3$ $mol^{-1}$ which is smaller than the $K_{SV}$ value of $^1AcrH_2{}^*$ ($1.2 \times 10^2$ $dm^3$ $mol^{-1}$).

The quantum yields ($\Phi$) of the photocatalytic dechlorination of ClBP were determined using a ferrioxalate actinometer. The $\Phi$ values in the presence of $AcrH_2$ under irradiation of light ($\lambda$ = 320 nm) were constant with the change of both $AcrH_2$ and $NaBH_4$ concentrations. On the other hand, the quantum yield increased with an increase in the concentration of ClBP to approach a limiting value ($\Phi_\infty$) in the high concentrations in accordance with Eq. 1. Then, from the linear plot between $\Phi^{-1}$ and $[\mathrm{ClBP}]^{-1}$ the

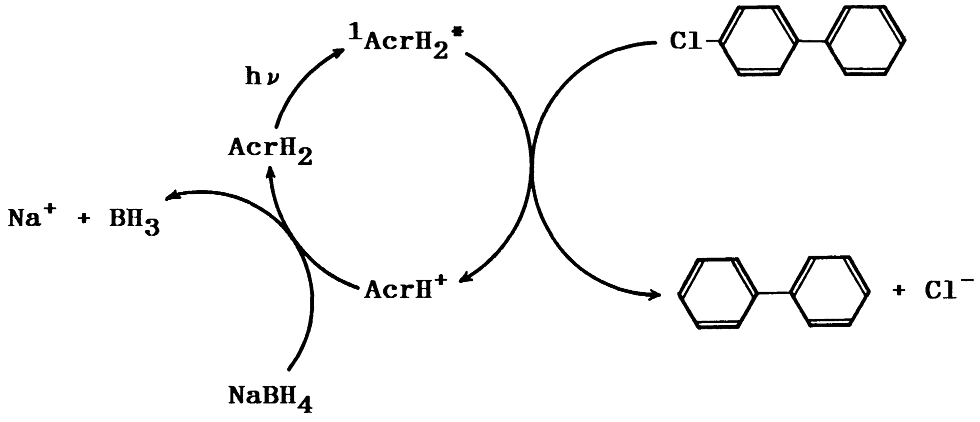
$$\Phi^{-1} = \Phi_\infty{}^{-1}[1 + (K_{obs}[\mathrm{ClBP}])^{-1}] \tag{1}$$

$\Phi_\infty$ and $K_{obs}$ values are obtained as 0.42 and 1.6 x $10^2$ $dm^3$ $mol^{-1}$, respectively. In the absence of $NaBH_4$ as well, p-chlorobiphenyl was reduced by $AcrH_2$ in MeCN/$H_2O$ (9:1 v/v) under irradiation of light ($\lambda$ = 320 nm) to yield $AcrH^+$ and biphenyl, Eq. 2. The $\Phi$ values in the absence of $NaBH_4$



(2)

showed the same dependence on the concentration of ClBP as Eq. 1, and the $\Phi_\infty$ and $K_{obs}$ values were determined as 0.61 and 1.2 x $10^2$ $dm^3$ $mol^{-1}$, respectively, which agree reasonably well as those obtained in the presence of $NaBH_4$ (0.42 and 1.6 x $10^2$ $dm^3$ $mol^{-1}$, respectively).[11] When $AcrH_2$ is replaced by $AFH^+$ in the photocatalytic reductive dechlorination of ClBP with $NaBH_4$, the limiting quantum yield ($\Phi_\infty$ = 0.63) becomes larger than the case of $AcrH_2$ ($\Phi_\infty$ = 0.42) under irradiation of light of longer wavelength ($\lambda$ = 350 nm), which has the sufficient overlap with the solar spectrum for the practical use. The $K_{obs}$ values obtained from the $\Phi$ dependence on the concentration of ClBP (Eq. 1) in the $AcrH_2/AcrH^+$- and $AFH_2/AFH^+$-catalyzed photo-dechlorination with $NaBH_4$ ($K_{obs}$ = 1.6 x $10^2$ and 3.3 x $10^1$ $dm^3$ $mol^{-1}$, respectively) agree well with the $K_{SV}$ values of ${}^1AcrH_2{}^*$ and ${}^1AFH_2{}^*$ ($K_{SV}$ = 1.2 x $10^2$ and 3.6 x 10 $dm^3$ $mol^{-1}$, respectively). Thus, the photocatalytic dechlorination of p-chlorobiphenyl by $NaBH_4$ may proceed via the reductive dechlorination of ClBP by the singlet excited states ${}^1AcrH_2{}^*$ (or ${}^1AFH_2{}^*$), followed by the thermal reduction of $AcrH^+$ (or $AFH^+$) by $NaBH_4$ to regenerate $AcrH_2$ (or $AFH_2$) as shown below.



References

1) "PCB Poisoning and Pollution," ed by K. Higuchi, Academic Press, Tokyo (1976); D. G. Ackerman, L. L. Scinto, P. S. Bakshi, R. G. Delumyea, R. J. Johnson, G. Richard, A. M. Takata, and E. M. Sworzyn, "Destruction and Disposal of PCBs by Thermal and Non-Thermal Methods," Noyes, Park Ridge (1983); I. Mori, Kankyo Gijutsu, 14, 588 (1985).

2) G. A. Epling, W. M. McVicar, and A. Kumar, Chemosphere, 17, 1355 (1988).

3) M. Ohashi, K. Tsujimoto, and K. Seki, J. Chem. Soc., Chem. Commun., 1973, 384; K. Tsujimoto, S. Tasaka, and M. Ohashi, ibid., 1975, 758; M. Ohashi and K. Tsujimoto, Chem. Lett., 1983, 423; Y. Tanaka, T. Uryu, M. Ohashi, and K. Tsujimoto, J. Chem. Soc., Chem. Commun., 1987, 1703.

4) J. Ph. Soumillion, P. Vandereecken, and F. C. De Schryver, Tetrahedron Lett., 30, 697 (1989).

5) N. J. Bunce, J. P. Landers, J. A. Langshaw, and J. S. Nakai, Environ. Sci. Technol., 23, 213 (1989); N. J. Bunce, C. T. DeSchutter, and E. J. Toone, J. Chem. Soc., Perkin Trans. 2, 1983, 859.

6) P. K. Freeman, R. Srinivasa, J.-A. Campbell, and M. L. Deinzer, M. L. J. Am. Chem. Soc., 108, 5531 (1986).

7) G. A. Epling and E. Florio, J. Chem. Soc., Chem. Commun., 1986, 185; G. A. Epling and E. Florio, Tetrahedron Lett., 27, 675 (1986).

8) Typically, an MeCN/$H_2O$ (9:1 v/v) solution (0.50 $cm^3$) containing ClBP (0.10 mol $dm^{-3}$) and $NaBH_4$ (1.0 mol $dm^{-3}$) was added to a quartz cuvette (1 mm i.d) and deoxygenated by a stream of argon. The photolysis with a Ushio model U1-501 Xenon lamp results in no appreciable reaction under our experimental conditions, although photolysis of ClBP and $NaBH_4$ with a low pressure mercury lamp is reported to result in the dechlorination of ClBP.<sup>7)</sup>

9) R. M. G. Roberts, D. Ostovic, and M. M. Kreevoy, Faraday Discuss. Chem. Soc., 74, 257 (1982).

10) The reductive debromination of bromochlorobenzenes proceeds more efficiently than the dechorination, since chlorobenzene is obtained as a major product; e.g., the product ratio of PhCl to PhBr was 8:1 in the case of o-$BrC_6H_4Cl$.

11) S. Fukuzumi and T. Tanaka, "Photoinduced Electron Transfer," ed by M. A. Fox and M. Chanon, Elsevier, Amsterdam (1988), Part C, Chap. 10.

12) The limiting quantum yields in the presence of $NaBH_4$ may be larger than 0.42, since the photolysis in the presence of $NaBH_4$ results in the formation of $H_2$ which bubbles up from the reactant solution, causing the slight decrease in the light absorption.

(Received April 9, 1990)