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PHOTODECHLORINATION OF CHLOROAROMATICS BY ELECTRON TRANSFER FROM AN ANIONIC SENSITIZER

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Summary: A novel photosensitized process for dechlorination of chloronaphthalene, chlorobiphenyl and, potentially, polychlorinated aromatics uses naphthoxide anion as excited donor. This process proceeds through the radical anion of the chloroaromatic and presents characteristics comparing favorably with other sensitized systems.

The widespread use of substituted haloaromatics as pesticides or electrical insulators is often accompanied by severe environmental problems. For this reason, research is needed to devise realistic ways for the degradation of these pollutants . The photochemistry of aryl halides appears as an interesting way for dehalogenating these molecules; the subject has been reviewed (1-4). The photodechlorination by direct irradiation of a chloroaromatic will always necessitate a case by case optimization. The energy absorbed, the nature of the excited precursors (4,5) and the intervention of exciplexes (6,7) or excimers (8), leading or not to dechlorination, are features changing from one molecule to the other.

Photodechlorination enhanced by an electron transfer mechanism is a more promising way and several attempts have already been published using aliphatic amines (9-12), anilines (13), anthracene (11), cyclohexadiene (12), borohydride (14) or hydroquinone (15). In this paper results obtained with an excited naphthoxide anion as sensitizer are presented. This process compares favorably with the preceeding systems.

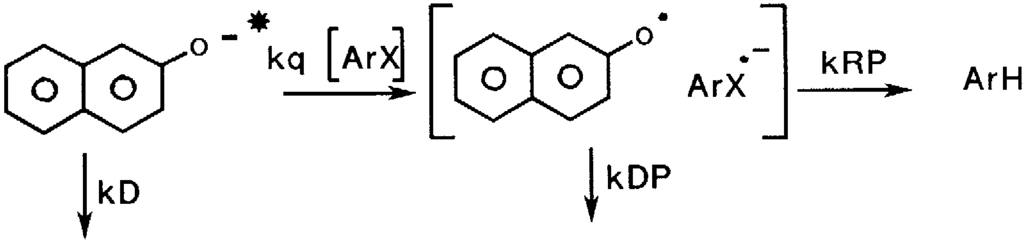
In the first runs, 2-chloronaphthalene (2CN) or 4-chlorobiphenyl (4CBP) solutions of ß-naphthol in methanol containing sodium hydroxide were irradiated around 3500 A. Results are presented in the table showing that the photoreduced products (ArH = biphenyl or naphthalene) account for about 70% of the disappeared chloroaromatic (ArCl). More interesting is the fact that the process works in a catalytic way even though, at the present time, turnovers are still low (between 3 and 10).

Table : Photodechlorinations of 2-chloronaphthalene (2CN) and 4-chlorobiphenyl (4CBP) sensitized by naphthoxide anion.

ArCl	2CN	4CBP
[Naphtol]o	$2\ 10^{-3}$ M	$2\ 10^{-3}$ M
[ArCl]o	$7.5\ 10^{-3}$ M	$7.5\ 10^{-3}$ M
[ArCl]t	$2.3\ 10^{-3}$ M	$3\ 10^{-3}$ M
[ArH]t	$3.8\ 10^{-3}$ M	$3\ 10^{-3}$ M
Yield (ArH)	73 %	66 %
ArX consumed	69 %	60 %
Naphthol consumed	25 %	70 %
Turnover	10	3.2

Solutions (3 ml) 0.04 M in NaOH, were irradiated during 4 hours,at room temperature and after freeze thaw degassing, in Pyrex tubes, i.d. 11 mm. Four RUL-3500 A°,RPR black light phosphor lamps (12 W) were used.

The excited state involved is the naphthoxide singlet since the results can be explained by the following kinetic scheme:



leading to the stationary equation:

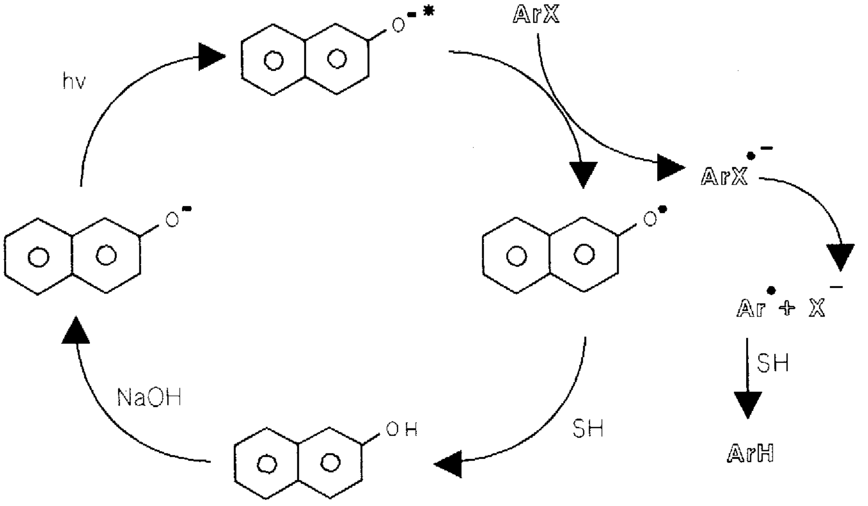
$$1/\Phi_p = kDRP/kRP + (kDRP/kRP.kSV).[ArX]$$

where Φ_p = quantum yield of biphenyl formation,
kDRP = kRP + kDP
kSV = kq/kD

A Stern-Volmer plot of Φ_p^{-1} versus $[4CBP]^{-1}$ gives a linear relation with a slope to intercept ratio of 56.5 $L.M^{-1}$. The naphthoxide fluorescence is quenched by the 4CBP molecule and this leads to the same value(60 $M.L^{-1}$) if the results are treated according to the Stern-Volmer equation.

That electron transfer is responsible for the quenching may be shown by the fact that the fluorescence quenching constants of the naphthoxide anion by various acceptors decrease with their reduction potentials. The quenching constants for 4CBP or 2CN correctly fit into the series.

The following scheme may explain the results:



This process presents several advantages over other photoreduction systems already tested. 1) The sensitizer is bathochromic relative to most of the chloroaromatics, allowing selective excitation. 2) The absorption spectrum of the naphthoxide anion fits very well with the emission of black light phosphor lamps, giving efficient light absorption. 3) With a quantum yield of about 0.3, this reaction compares favorably with direct irradiation: CBP's lacking ortho chlorine substituents have quantum yields of about 10^{-3} (16). 4) The electron donor is catalytically regenerated 5) The reaction can proceed to complete disappearance of chloroaromatic and it was verified that 100 % of the disappeared organic chlorine is recovered as sodium chloride. 6) Chlorobiphenyl may be extensively dechlorinated although it is the least efficient acceptor in the polychlorobiphenyl series. Photoreduction of other chlorinated compounds may be foreseen on the basis of their reduction potentials: we have shown that the process works with dichlorinated benzenoid compounds and with monochlorinated naphthalenes or biphenyls.

Due to the electron transfer mechanism of quenching, the dehalogenated product (ArH), being a poorer acceptor, will not compete very efficiently with the starting ArX even at high conversion.

The low turnovers may be related to several secondary reactions like radical coupling between naphthoxy radicals or between naphthoxy and aryl radicals. This last process may occur if the chloride anion is released while the radical anion remains in the solvent cage (17). On the other hand, the occurrence to a certain extent of $S_{RN}1$ substitution, where naphtoxide anion adds to the aryl radical, cannot be completely excluded (18) . The side products of the reaction have not yet been identified but LC/MS analysis of the mixture agrees with products whose m/e value corresponds to the coupling between aryl and naphthoxy radicals. Optimization experiments to enhance the catalytic cycle are now in progress.

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