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Photosensitizers covalently anchored to the silica surface: enhanced efficiency of heterogeneous photodechlorination of chlorinated aromatics.

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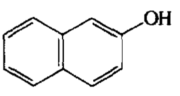
Abstract: A naphthol sensitizer is covalently anchored on silica. The so obtained heterogeneous as well as the corresponding homogeneous photosensitizer, under anionic form, have been tested in the reductive dechlorination of chloroaromatics. In these photoinduced electron transfer (PET) sensitized reactions, interactions between the sensitizer and the surface are shown to enhance their reactivity. The grafted silica is shown to work in the dechlorination of a tetrachlorobiphenyl and sunlight reactions have been performed.

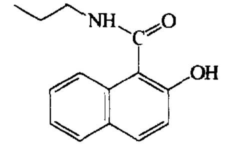
Sensitizers attached at the surface of silicagel by a covalent link have been the subject of several recent papers [1-3]: they may be used with an efficiency comparable to the one observed in the homogeneous liquid phase. Besides the ease of separating the photoproduct from the anchored sensitizer, the modulation of the sensitizer efficiency linked to the properties of the surface have been underlined [4].

Photodehalogenation under sunlight is important for the environmental detoxification of haloaromatic compounds. Their photochemistry been studied and reviewed [5-8]. Among various ways for dechlorination, the photoinduced electron transfer (PET) mechanism has been proposed [9] and new systems were still recently presented [10-11]. We have shown that the naphtoxide anion sensitizer works in an efficient way, acting as a renewable sensitizer and leading to complete dechlorination [10]. In the line of this research, an heterogeneous version of our process, using a naphtholate sensitizer covalently anchored on silica, is presented in this paper.

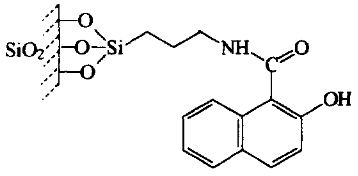
A naphthol sensitizer has been anchored on a silica support through an amide bond, using commercially available 2-hydroxynaphthoic acid and 3-aminopropyl silicagel. The N propyl amide of the 2 hydroxynaphthoic acid was prepared as well in order to allow comparisons between homogeneous and heterogeneous photodechlorinations. The compared sensitizers are shown below.



NOH



ANOH



$ANOH

The 2-chloronaphthalene (2-ClN) has been choosen for testing the dechlorinations (see table 1).

Table 1: Dechlorination of 2 chloronaphthalene (2-ClN) photoinduced by excited naphtholate anions [a]

Sensitizer [b]	Irradiation time(hours)	[2-ClN]o	[2-ClN] consumed	[N] [c] formed	Dechlorination (%) [d]
NOH	1.15	6.6	2.3	1.6	34
ANOH	1.15	6.9	0.24	0.27	4
ANOH	9	7	0.98	1.03	14
$ANOH	9	6.7	1.12	0.83	17

a) Irradiation by a set of 3 RUL-3500 Å RPR Black light phosphor lamps (12 W) placed at 10 cm of the samples. Volumes were 5 ml in methanol solvent. Samples were degassed for 1.5 hour before irradiation. All concentrations x 10^3 M

b) [NOH]o = [ANOH]o = 3.10^{-3} M. [NaOH]o = 40.10^{-3} M. [$ANOH]o = 15 mg suspended in the solution which corresponds to a sensitizer concentration of 1.67 10^{-3} M as a maximum.

c) N = naphthalene. Accuracy of the concentration measurements is ± 0.02

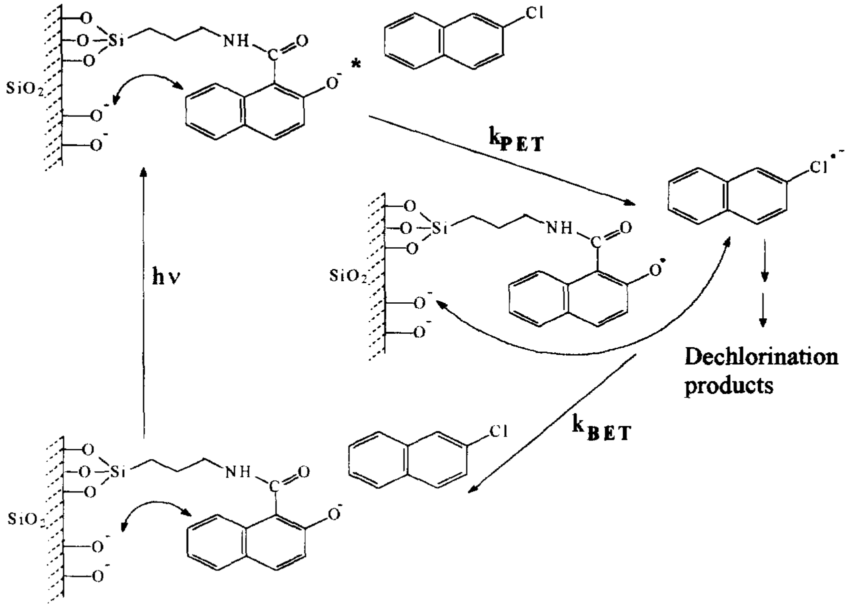
d) Calculated versus engaged 2-ClN

As shown, the ANOH sensitizer is less efficient than NOH and this may be expected. Firstly, the λ_{max} (360 nm) of the ANO$^-$ is found bathochromic versus NO$^-$ (350 nm), due to some conjugation with the amide function. Secondly, hydrogen bonding stabilisation of ANO$^-$ by the ortho amide function is expected. The decrease of efficiency of ANO$^-$ versus NO$^-$ is showing up in the fluorescence quenching of the naphtholate anions by 2-ClN: a Stern Volmer constant of 49 M^{-1} has been measured [12] for the NO$^-$ while for ANO$^-$ it is not measurable. The absence of fluorescence quenching means that the ANO$^-$ photoinitiated reaction is a triplet sensitized reaction.

A comparative photodechlorination of 4 chlorobiphenyl (4ClB), 2-ClN and pentachlorobenzene ($PhCl_5$) has been run using ANO^-$: the dechlorination percentages, calculated as in table 1 were respectively 0.9, 2.7 and 13 %. This follows the order of the chloroaromatic reduction potentials (Ered (V) = -2.37 [13], -2.3 [14], -1.92 [15] respectively, in acetonitrile vs SCE). We believe that the reaction mechanism is a triplet state electron transfer quenching. However, it should be noted that $PhCl_5$ quenches the ANO^-$ fluorescence and that some singlet sensitized reaction may occur in this case.

When comparing the dechlorinations initiated by $ ANO$^-$ and ANO$^-$, the grafted sensitizer is found more efficient than the corresponding homogeneous one: its concentration is weaker in the case of the heterogeneous reaction and the dechlorination yield is higher. Moreover, about two thirds of the grafted naphtholates were found to be inactive: when $PhCl_5$ is used as a quencher of the $ANO⁻ fluorescence, only one third of the excited states are quenched and the residual fluorescence is found insensitive to a further increase of the $PhCl_5$ concentration. This probably means that the unquenched $ANO⁻ chromophores are unaccessible sensitizers located in cavities which are too small for accepting quencher molecules.

This implies that the anchored sensitizer is several times more reactive than the corresponding homogeneous molecule. The increased efficiency may be explained in the following way: the negatively charged naphtholate is probably moved away from the silica surface by electrostatic repulsions due to the residual silanolates. Furthermore, the same electrostatic interactions are probably repelling the radical anion obtained after the PET from the excited naphthoxide has taken place: as a result, back electron transfer (BET) to the initial state is decreased and the photoreaction yield is increased (see scheme below). A similar explanation has already been given in a system where a PET reaction was performed at the surface of silicagel suspended in basic solution [16].



The usefulness of this heterogeneous sensitizer has been tested in the photodechlorination of 3,4,3',4' tetrachlorobiphenyl (TCB), showing that it may be used in the case of PCB's (polychlorobiphenyls). The dechlorination yield is high and the heterogeneous sensitizer is regenerated with a turnover larger than 8 (table 2).

In a last series of experiments, sunlight dechlorination of 2-ClN has been shown to work: a 5 % dechlorination was obtained after a two (Belgian cloudy) days exposure of a pyrex tube containing an initial 2-ClN concentration of $6.6\ 10^{-3}$ M. This corresponds to a rate decrease by a factor of 10 when compared to the irradiations of table 1. Experiments are under progress in order to improve this sensitizing system.

Table 2 : Dechlorination [a] of 3,4,3'4' tetrachlorobiphenyl (TCB), photoinduced by excited \$ANO^{-} [b]

Irradiation time (Hours)	[NaOH] consumed [c]	[TCB] consumed	Dechlorination % [d]
26	14.0	5.6	44
62	28.5	7.9	90

a) Irradiation conditions as for table 1 excepting degassing (2.5 hours). All concentrations x 10^{3} M

b) [\$ANOH]o = 30 mg which gives a sensitizer concentration of 3.3 10^{-3} M as a maximum; [NaOH]o = 40.10^{-3} M; [TCB]o = 7.9 10^{-3} M.

c) Sodium hydroxide has been measured by HCl titration. In all dechlorinations, the NaOH consumption exactly matches the chloroaromatic disappearance and the corresponding chloride anion formation.

d) Calculated through the NaOH consumption. HPLC measurement shows biphenyl and residual 4-chlorobiphenyl, a dichlorobiphenyl and traces of two trichlorobiphenyls.

Experimental: *ANOH:* synthesized from 2-hydroxynaphthoic acid (10 mmol), N,N dicyclohexylcarbodiimide (10 mmol) and propylamine (14 mmol) in dichloromethane (60 ml), stirred 2 hours at 0°C and 8 hours at 20°C. The product is isolated and purified by silicagel chromatography and recrystallization in hexane. Yield: 50% . M.P.: 111°C. ^{1}H NMR: 1.2 (t, 3H); 1.8 (m, 2H); 3.7 (t, 2H); 6.6 (m, 1H); 7.3-8.4 (m, 6H); 11.6 (s,1H). Anal. Found %: C, 73.34; H, 6.48; N, 6.10. Calc. %: C, 73.34; H, 6.54; N, 6.10.

\$ANOH: 3-Aminopropylsilicagel (Aldrich) dried under vacuum at 80°C for 10 hours was suspended in anhydrous toluene with 2-hydroxynaphthoic acid and N,N-dicyclohexylcarbodiimide. After stirring at room temperature for 2 days, the grafted silica is separated, washed in a Soxhlet with toluene, methanol, ethanol, ether and dried as preceedingly under vacuum. Elemental analysis (% C, 10.35; % N, 1.16) gives a maximum loading of 5.5 10^{-4} mole/g..

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