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PHOTO-ENHANCED REDUCTION OF CARBONYL COMPOUNDS BY SODIUM BOROHYDRIDE

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Abstract: The reduction of ketones and some esters by sodium borohydride is dramatically accelerated by uv irradiation. The reaction seems to proceed from the (n, π^*) excited state of the carbonyl compound. The photocatalytic effect is dependent on the solvent polarity and substituents on aromatic carboxylic acids and alcohols of esters.

Witkop and his coworkers have found in 1965 for the first time that photoexcitation of heterocyclic compounds enhance the sodium borohydride reduction.[1] They have also observed that the rate of the photoreduction of steroidal ketones by sodium borohydride was enhanced.[2] It has recently been reported that cyclohexanones were reduced nearly quantitatively to cyclohexanols with sodium borohydride by photoexcitation in diglyme solvent in which the compound is inert or very slowly reduced without irradiation, and the reduction of ketones by sodium borohydride in general was dramatically accelerated by irradiation.[3] In addition esters such as methyl benzoate and methyl cyclohexanecarboxylate, were reduced in 90% conversion to the corresponding alcohols by uv irradiation either in alcoholic solvents or in diglyme while esters are hardly reduced thermally by sodium borohydride in diglyme. Stimulated by these results we examined the photo-enhanced borohydride reduction of carbonyl compounds in detail by studying the effect of solvents and substituents on the aromatic ring of the carbonyl compounds.

The quantum yields of ketones by sodium borohydride in diglyme are summarized in Table I. Aliphatic ketones showed larger quantum yields than aromatic ketones. The excitation of aromatic ketones by 254 nm uv light generates both (n, π^*) and (π,π^*) states, mainly (π,π^*) state, while (n,π^*) configuration exerts the major contribution to the excited state in aliphatic ketones. The results suggest that the photoreduction of ketones by sodium borohydride proceeds mainly from (n,π^*) excited states. The larger quantum yield of photoreduction of benzophenone at 366 nm (0.99) compared to that at 254 nm (0.14) supports the suggestion since the excited state of benzophenone at 366 nm is mainly (n,π^*) character.

Table I. Quantum yields of photoreduction of ketones by sodium borohydride in diglyme at 254 nm.

Compounds	Quantum yields
Acetophenone	0.07
	0.01^a
2'-Acetonaphthone	0.10
Benzophenone	0.14
	0.99^b
2-Butanone	0.25
4-Methyl-2-pentanone	0.21

[a] At 313 nm. [b] At 366 nm.

Table II. Quantum yields of photoreduction of methyl benzoate by sodium borohydride at 254 nm in various solvents.

Solvents	Quantum yields
Isopropyl alcohol	0.07
Dimethylformamide	0.03
Dimethylsulfoxide	0.04
Ethanol	0.08
Diglyme	0.50

The photo-enhanced reduction of esters is systematically studied varying the solvents and substituents. In a typical experiment, 0.2g of $NaBH_4$ (about 0.005 mole) was dissolved in about 40 ml of solvent in a 50 ml volumetric flask, and 0.68g methyl benzoate (0.005 mole) was added and diluted to 50 ml with the solvent. A portion of this solution (3 ml) was transferred by a syringe into a quartz tube capped with rubber septum and irradiated in a merry-go-round for 2 hrs with 254 nm light through the filter solution. After irradiation, 2 ml of the reaction mixture was transferred into 5 ml volumetric flask and added 1 ml of 6N H_2SO_4 solution to destroy the unreacted borohydride. After H_2 gas evolution ceased, the solution was neutralized with concentrated aqueous Na_2CO_3 solution and diluted to 5 ml with distilled water, then the amount of benzyl alcohol produced was determined by glc analysis. An irradiated blank solution (2 ml) was treated by the same procedure and analyzed by glc for a control. Quantum yields were determined utilizing tris(oxalato)ferrate actinometry, purified benzyl alcohol as a glc standard, and Carbowax 20M 6'x1/8" column. The results are summarized in the Tables.

The quantum yields of photoreduction of methyl benzoate by sodium borohydride are dependent on solvents as the reaction rates vary with the solvents used as shown in Table II. Quantum yields decrease as the polarity of the solvents increase. These results also suggest the reaction to proceed via the (n, π^*) excited state. However, the polarity of the reaction mixture in this system is difficult to define because the ions of Na^+ and BH_4^- change the polarity of the solution. Consequently, there would be some difficulties in defining the diglyme solution as nonpolar. In general, the lowest excited state of aliphatic carboxylate derivatives is (n, π^*) but in aromatic carboxylate derivatives, the

Table III. Quantum yields of photoreduction of esters by sodium borohydride in diglyme at 254 nm.

Compounds	Quantum yields
Methyl benzoate	0.50
Methyl 4-methoxybenzoate	0.03
Methyl 2-chlorobenzoate	0.50
Methyl 4-nitrobenzoate	0.05
Methyl 2-furancarboxylate	0.01
Ethyl 5-methyl-4-imidazolecarboxylate	<0.01

Table V. Quantum yields of photoreduction of benzoic acid sodium salts by sodium borohydride in aqueous alkaline solution at 254 nm.

Compounds	Quantum yields
Benzoic acid salt	<0.001
4-Methoxybenzoic acid salt	<0.001
2-Chlorobenzoic acid salt	<0.001
4-Nitrobenzoic acid salt	<0.001
2-Furancarboxylic acid salt	<0.001

Table IV. Quantum yields of photoreduction of benzoic acids by sodium borohydride in diglyme at 254 nm.

Compounds	Quantum yields
Benzoic acid	<0.01
2-Chlorobenzoic acid	<0.01
4-Methoxybenzoic acid	<0.01
4-Nitrobenzoic acid	<0.01
2-Furancarboxylic acid	<0.01

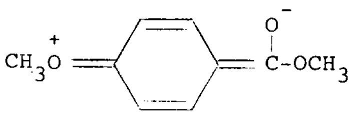
Table VI. Quantum yields of photoreduction of phenyl cyclocarboxylate by sodium borohydride in diglyme at 254 nm.

Cyclohexanecarboxylic acid esters	Quantum yields
Methyl	0.3
Phenyl	1.0
2-Chlorophenyl	3.0
4-Chlorophenyl	4.0
2-Methylphenyl	0.4
3-Methylphenyl	0.2
4-Methylphenyl	0.7
4-Methoxyphenyl	0.1

lowest excited state is generally (π, π^*) state. Hence it is hard to rule out the reactive (π,π^*) excited state from this solvent effect only.

Since the quantum yield of photoreduction of methyl benzoate by sodium borohydride is the largest, we measured the quantum yields of reduction of various aromatic acid derivatives employing diglyme as a common solvent. Neither the aromatic acids nor the sodium salts of these acids are reduced even though the compounds are photoexcited. The photoreduction of carboxylate anions with sodium borohydride is not expected to occur since carboxylate anions generally eject electrons by photoexcitation.[4] In ester, the ether oxygen has two effects; it withdraws electron through the σ bond framework making the carbonyl oxygen electron deficient and it is also a π electron donor which would make the carboxyl oxygen electron rich. Since σ withdrawal is more efficient than π donation for oxygen, the net result is the formation of an electrophilic excited state.

In the photochemical reduction of esters by sodium borohydride in diglyme solution, methyl benzoate and methyl 2-chlorobenzoate with (n, π^*) state as the lowest excited state show the large quantum yields while methyl 4-methoxybenzoate and methyl 4-nitrobenzoate with the lowest (π, π^*) excited state show the small quantum yields. In the excited state, 4-methoxy substituent of aromatic ring will become strong electron donating group as in the case of excited phenol.[5] This effect increases the electron density of carbonyl carbon of esters and thus electron or hydride capture is inhibited, and the contribution of the charge transfer structure (I) in the excited state of methyl 4-methoxybenzoate will reduce the reduction quantum yield.



(I)

When the phenolate moiety absorbs the light rather than the carboxylic acid moiety in the photoreduction of cyclohexanecarboxylic acid esters, the reduction is very much enhanced as shown by large quantum yields. In chlorophenyl esters, certain radical chain process seems to be involved since the quantum yields of photoreduction are higher than 1 in 2-chlorophenyl and 4-chlorophenyl cyclohexanecarboxylates. Probably initial C-Cl homolysis is involved.

The following conclusions can be drawn from the results of the photoreduction of esters and ketones by sodium borohydride: 1) the reduction quantum yields are larger in nonpolar solvents than in polar solvents; 2) the reduction of methyl cyclohexanecarboxylate and ketones proceeds from the lowest excited (n, π^*) state; 3) for the compounds whose lowest excited state is (π,π^*) state, the photo-acceleration of reduction by sodium borohydride in diglyme is negligible.

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