A Link between Photoreduction and Photosubstitution of Chloroaromatic Compounds

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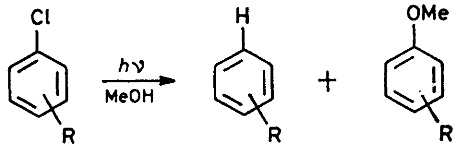
Summary The photoreaction of chloroaromatic compounds in methanol is explained by a mechanism which includes electron transfer from the triplet to the ground state of the substrate.

We have studied the photoreduction of chlorobenzene and chloroanisoles, especially under conditions in which photoreduction and photosubstitution occur simultaneously (Scheme 1);[1] methanol, the solvent, acts as a hydrogen donor and as a nucleophile.

The Table summarizes our results and shows that photoreduction is the main process in the majority of cases.



R = H or OMe

Scheme 1

As expected, when sodium cyanide is present in the medium a nitrile is obtained and its formation occurs at the expense of the other products. The *para*-orienting effect of the methoxy-group[2] is also observed; the quantum yield of

Table. Photochemical reduction and substitution in methanol.

Expt.	R[a]	[ArCl] M × 10^2	Additive (M)	Conversion %	$h\nu$[b]	ArH %	ArOMe %	ArCN %	ArH/ ArOMe
1	H	6·38		11	1	77	19		4·1
2	H	5·81	CN^-(0·06)	29	1	57	9	1	
3	H	6·38		0	2				
4	H	6·38	Me_2CO(0·76)	5	2	62	36		1·7
5	H	6·38	Me_2CO(1·91)	11	2	43	21		2
6	*p*–OMe	3·77		31	1	79	13		6·1
7	*p*–OMe	3·75	CN^-(0·19)	30	1	4	5	89	
8	*p*–OMe	3·77	Me_2CO(0·57)	17	1	79	21		3·7
9	*p*–OMe	3·77	Me_2CO(2·29)	18	1	59	19		3·1
10	*m*–OMe	5·07		60	1	71	22		3·2
11	*m*–OMe	5·07	CN^-(0·07)	26	1	49	16	4	
12	*m*–OMe	4·3	Me_2CO(2·04)	49	1	41	37		1·1
13	*m*–OMe	4·3	Me_2CO(2·04)	49	2	34	52		0·7

[a] R in $-C_6H_4R(\equiv Ar)$; *o*-chloroanisole gave only reduction products in methanol. [b] 1 = low-pressure mercury lamps, quartz reactor; 2 = medium-pressure mercury lamps, Pyrex reactor.

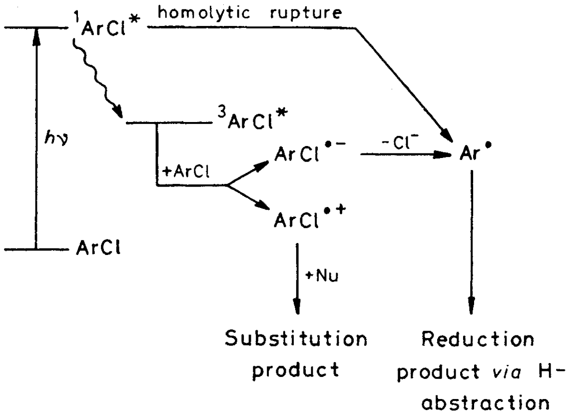
the reaction of *p*-chloroanisole is enhanced by the introduction of cyanide and the cyano-product is predominant (Expts. 6 and 7).

Since we observed that the fluorescence of chloroaromatic compounds is not quenched by cyanide, the singlet state is not the species interacting with this nucleophile. On the other hand, sensitization experiments (acetone sensitizer) show that both substitution and reduction arise from the triplet state (Expts. 4 and 5, 8 and 9, and 12 and 13).

It is important to note that the distribution of the product ratio (reduction *vs.* substitution, *i.e.* ArH *vs.* ArOMe) changes when passing from direct to sensitized photolysis. In all cases, the triplet precursor affords an increased amount of substitution product. This difference implies that the singlet state also gives the reduction product.

Since the reduction product arises from the two excited states, a problem appears; the C–Cl bond is not expected to be broken homolytically in the triplet state since the triplet energies of chlorobenzene (82 kcal mol^{-1})[3] or the chloroanisoles[4] are too low (*D*PhCl 86 kcal mol^{-1}).[5]†

Therefore, we propose a new mechanism (Scheme 2) which rationalizes these results and is, possibly, a general pathway for photoreduction and photosubstitution. The formation of a pair of radical-ions *via* a triplet excimer is a key step. The precursor of the reduction product, which arises from the triplet state, would be a radical-anion, thus avoiding the energy demanding homolysis. The radical-cation is postulated as the precursor of the substitution product. Ionization of the triplet state to give the solvated electron[6] does not seem, in the absence of water, likely. On the other hand, oxygen, a very efficient quencher of solvated electrons, does not affect the results.



SCHEME 2. ^{1}Ar = singlet state, ^{3}Ar = triplet state.

Finally, it must be noted that, for chlorobenzene, an emission which arises from a triplet excimer can be observed[7] and that the participation of excimers has been invoked in the photodechlorination of chloronaphthalenes.[8,9]

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† 1 cal = 4·184 J.

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