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Selectivity in photohydroxylation of 4-nitroveratrole and nitroanisoles catalysed by cyclodextrins

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Abstract

Photohydroxylation of 4-nitroveratrole in the presence of cyclodextrins results in regioselective formation of 2-methoxy-4-nitrophenol as the exclusive product. This is in contrast to solution photolysis, wherein isomeric 2-methoxy-5-nitrophenol is the sole product. Similarly cyclodextrin complexation of 2-nitro- and 4-nitroanisoles, upon photohydroxylation, results in displacement of nitro group, in contrast to solution photolysis in which mixture of nitro- as well as methoxy-displaced products are obtained. The observed results are explained as due to an increase in the local concentration of the nucleophile, upon cyclodextrin encapsulation. This active participation by cyclodextrins in photohydroxylation causes a shift in reaction mechanism from a direct displacement route (S_N2Ar^*) to one involving electron-transfer ($S_N(ET)Ar^*$) pathway.

Keywords: 4-Nitroveratrole; Nitroanisoles; Photohydroxylation; Cyclodextrin complexation

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides containing six, seven or eight glucose units and are called α-CD (cyclohexaamylose), β-CD (cycloheptaamylose) and γ-CD (cyclooctaamylose), each having a different cavity diameter of approximately 4.5, 7.0 and 8.5 Å units respectively. They are well-known host molecules finding extensive use in complexation and catalysis studies [1]. With well-defined cavities, small size and ease of functionalisation, they also serve as useful enzyme models [2]. CD complexation of guest molecules exhibits remarkable selectivity and catalysis in many thermal [3] and photochemical reactions [4] of guest molecules, as CD can geometrically constraint the guest, stabilize conformations that are less favoured in solution and regulate the traffic of the incoming reagents towards certain accessible positions of the entrapped species by encircling and protecting the rest of the reactive sites.

Since their discovery in 1956, photo-induced nucleophilic substitution reactions of aromatic molecules have been receiving widespread attention. An earlier study [5] has shown that the photohydrolysis of 4-nitroanisole in 0.1 M NaOH gives 4-nitrophenol and 4-methoxyphenol in 1:4 ratio. de Vries [6] has studied photohydrolysis of 2-nitroanisole in which about 31% of 2-nitrophenol and 3% of guaiacol are isolated. The hydrolysis of 4-nitroveratrole has been studied by Stratenus [7]. Irradiation of a solution of 4-nitroveratrole in 0.01 M NaOH in water containing 2% THF affords exclusive formation of 2-methoxy-5-nitrophenol (**1b**) and no 2-methoxy-4-nitrophenol (**1c**) has been identified. But in the thermal hydrolysis of 4-nitroveratrole, (**1c**) is reported as the exclusive product. In another study [8] also, photohydrolysis of 4-nitroveratrole in 0.034 mM of NaOH has been reported to yield (**1b**) as the exclusive product and no (**1c**) is detected.

Havinga and de Jong [9] have shown that photosubstitution of hydroxyl group in 3-nitroanisole and 4-nitroanisole (**3a**) takes place at methoxy group and 3-nitroanisole is more reactive than 4-isomer. This also suggests that in this photochemical reaction, the methoxy group is more labile than the nitro group and the nitro group has a *meta* directing influence towards the nucleophilic substitution in the reactive excited triplet state. These interesting features, coupled with our interest in employing CDs as "microscopic reaction vessels" in achieving selectivity in photochemical reactions have prompted us to investigate the effect of CDs on photohydroxylation of 4-nitroveratrole and isomeric nitroanisoles and the results are presented below.

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2. Experimental

2.1. Materials

4-Nitroveratrole (Merck), α- and γ-CDs (American Maize) and β-CD (Aldrich) were used as received. 2-Nitroanisole (**2a**) and 4-Nitroanisole (**3a**) were recrystallised before use and their purity was checked by their melting point and also by gas chromatography. Tetrahydrofuran was doubly distilled and sodium hydroxide solution was prepared using doubly distilled water. For irradiations, a SAIC made, pyrex-filtered, photoreactor with 400 W medium pressure Hg vapour lamp was used.

2.2. Preparation of CD complexes

To a saturated solution of CD in water, equimolar amount of the substrate dissolved in minimum amount of methanol was added and stirred for 12 h at room temperature. The resultant white crystalline precipitate was filtered, washed with diethyl ether to remove any uncomplexed guest molecule and dried in an air oven for 6 h at 50 °C and the white crystalline powder was used for further studies.

2.3. Photohydroxylation

Sodium hydroxide solution was prepared by dissolving it in THF–water mixture and the pH was maintained at 11 (Systronics Digital pH meter). For solution irradiations in the absence of CDs, 20 ml of the above NaOH solution was used and the concentration of 4-nitroveratrole and nitroanisoles was fixed at 0.003 M. For irradiation of CD complexes, 0.1 g of 1:1 complex was thoroughly mixed with small amount of the NaOH stock solution into a paste form, which was subjected to irradiation for 3 h using a 400 W medium pressure mercury vapour lamp. After irradiation, the complex was dissolved in excess water and then extracted with hot chloroform. The concentrated solution was analysed by capillary GC.

2.4. Analytical methods

Samples were analysed by gas chromatography (Shimadzu 17A) using SE-30 10% capillary column, FID detector and high purity N_2 as carrier gas. In all the cases, retention times of the starting materials were taken as the internal reference. Products of the reaction were isolated by column chromatographic separation of the reaction mixture, carried out in bulk quantity. They were identified in GC (by co-injection with the reaction mixture) and also by their ^{1}H-NMR data (200 MHz, 25 °C, TMS).

Spectral data of photoproducts:

2-Methoxy-5-nitrophenol (**1b**): ^{1}H NMR ($CDCl_3$) δ (ppm): 7.92 (q, 1H); 7.28 (s, 1H); 7.0 (d, 1H); 6.2 (s, 1H) 4.00 (s, 3H).

Table 1
Formation constants[a] (K_f) of 4-nitroveratrole, 2-nitroanisole and 4-nitroanisole in cyclodextrins

Substrate	K_f ($dm^3\,mol^{-1}$)		
	α-CD	β-CD	γ-CD
4-Nitroveratrole (**1a**)	541	376	352
2-Nitroanisole (**2a**)	152	142	121
4-Nitroanisole (**3a**)	293	206	205

[a] Measured in 0.02% methanol–water mixture at room temperature from UV absorption data using Benesi–Hildebrand equation [10].

2-Methoxy-4-nitrophenol (**1c**): ^{1}H NMR ($CDCl_3$) δ (ppm): 7.72 (q, 1H); 7.28 (s, 1H); 7.0 (d, 1H); 6.2 (s, 1H) 4.00 (s, 3H).

2-Nitrophenol (**2b**): ^{1}H NMR ($CDCl_3$) δ (ppm): 10.59 (s, 1H); 8.14 (d, 1H); 7.59 (t, 1H); 7.18 (d, 1H); 6.95 (t, 1H).

2-Methoxyphenol (**2c**): ^{1}H NMR ($CDCl_3$) δ (ppm): 6.77 (s, 4H); 4.67 (s, 1H); 3.76 (s, 3H).

4-Nitrophenol (**3b**): ^{1}H NMR ($CDCl_3$) δ (ppm): 7.4 (d, 2H); 6.9 (d, 2H).

4-Methoxyphenol (**3c**): ^{1}H NMR ($CDCl_3$) δ (ppm): 6.77 (s, 4H); 4.67(s, 1H); 3.76 (s, 3H).

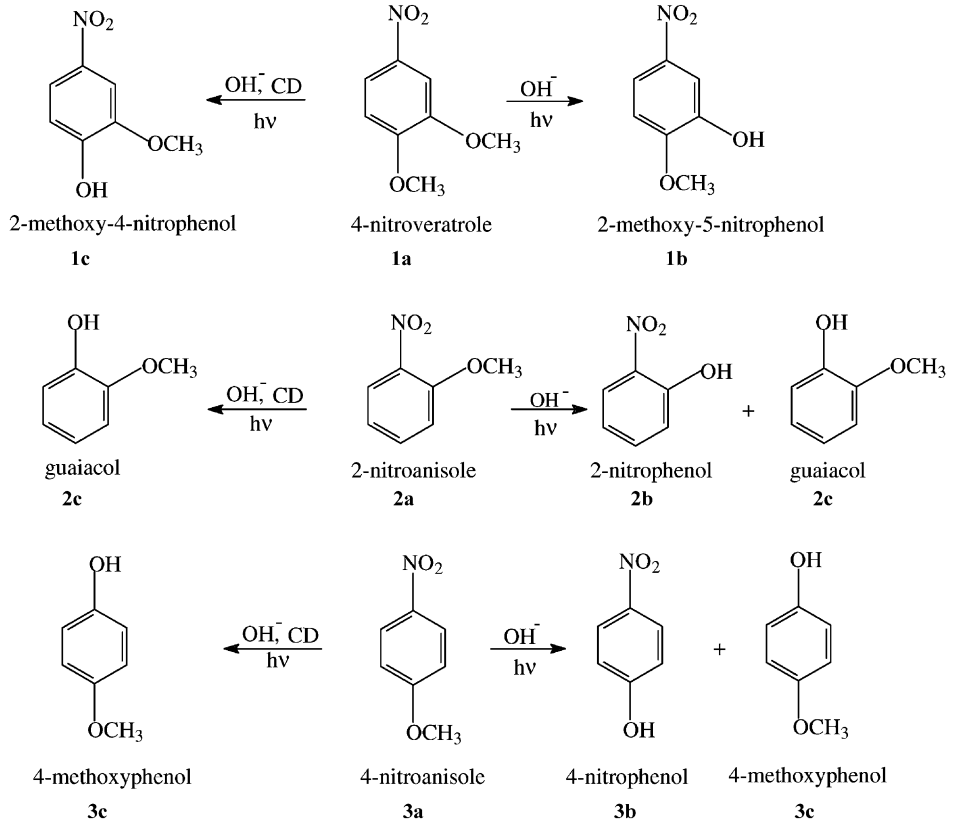
2.5. Determination of formation constants

Complex formation was inferred by evaluating the formation constants (K_f) using Benesi–Hildebrand method [10]. Stock solutions of 4-nitroveratrole and nitroanisoles (1×10^{-3} M) were prepared by weighing known amount of them and dissolving in 2% methanol–water mixture. 0.1 ml of this stock solution was transferred into a 10 ml volumetric flask, the respective CD (from a 0.01 M freshly prepared stock solution in water) was added, diluted to 10 ml with water and stirred for 6 h to ensure equilibrium in complexation. The absorption spectrum was recorded using a JASCO 7800 UV/Vis spectrophotometer and the absorption maxima for (**1a**), (**2a**) and (**3a**) are 340, 320 and 316 nm, respectively. The formation constants of various nitroaromatics with different CDs are presented in Table 1.

3. Results and discussion

Photohydroxylation of 4-nitroveratrole, 2- and 4-nitroanisoles are carried out in solution (1:9 THF–water mixture) and also as their complexes with α-, β- and γ-CDs. Photolysis of (**1a**) in isotropic medium in the presence of alkali results in exclusive formation of (**1b**), in which the methoxy group *meta*- to the nitro group is displaced (Scheme 1, Table 2).

However, when photolysed as α-, β- and γ-CD complexes, a remarkable alteration in selectivity is observed. Isomeric (**1c**), in which the methoxy group *para*- to the nitro group is displaced, is obtained as the exclusive product (which is the same product obtained in the thermal reaction between 4-nitroveratrole and NaOH).



Scheme 1.

Photohydroxylation in solution of 2-nitroanisole (**2a**) (Table 2) yields a mixture of 2-nitrophenol (**2b**) and guaiacol (**2c**) and of 4-nitroanisole (**3a**) yields 4-nitrophenol (**3b**) and 4-methoxyphenol (**3c**). This is in accordance with earlier reports [5,6]. However, photolysis of (**2a**) as its CD complex yields about 99% of (**2c**) and <1% of (**2b**). Similarly, the corresponding reaction of (**3a**) yields only (**3c**) and no (**3b**) when encapsulated in CDs. Thus, in nitroanisoles, a significant reduction in methoxy-substituted product and exclusive formation of the nitro-displaced product takes place and the same products are obtained in all the three CDs. In addition, the reaction in CDs is considerably faster than the solution phase reaction as evident from the increase in yield of photoproducts. It is also interesting to note that with all the three substrates, an increase in cavity size from α-CD to γ-CD, causes an increase in percentage conversion indicating that steric constraints around the reaction centre affects the reaction rate significantly.

Table 2
Products distribution in photohydroxylation[a] of 4-nitroveratrole, 2- and 4-nitroanisoles in solution and upon CD complexation

Substrate	Medium	(**a**)[b] (%)	(**b**) (%)	(**c**) (%)
4-Nitroveratrole (**1a**)	THF–water (1:9)	80	20	–
	α-CD	85	–	15
	β-CD	80	–	20
	γ-CD	70	–	30
2-Nitroanisole (**2a**)	THF–water (1:9)	90	7.5	2.5
	α-CD	75	–	25
	β-CD	60	trace	40
	γ-CD	22	trace	78
4-Nitroanisole (**3a**)	THF–water (1:9)	75	9.0	16
	α-CD	10	–	90
	β-CD	11	–	89
	γ-CD	5	–	95

[a] Irradiated for 3 h; products were analysed by GC; Error limit ±5%.
[b] For structures of (**a**), (**b**) and (**c**) refer Scheme 1.

Complexation with CDs is inferred from a comparison of the proton chemical shifts in ^{1}H-NMR data of CD complexes with the uncomplexed free CD[2] and also from the fairly high values in formation constants (Table 1) for all the three CDs calculated from UV absorption data [10] (with all the three substrates, addition of CDs causes an increase in ε_{max} without affecting the λ_{max} values). K_f values are highest with

[2] Comparison of the chemical shifts of α-, β- and γ-CD protons in the uncomplexed and complexed forms indicate that, while H-1, H-2, H-4 and H-6 protons are unaffected as a result of complexation, the H-3 and H-5 protons which are oriented towards the interior of the cavity undergo considerable upfield shifts. This chemical shift behaviour reflects complexation of 4-nitroveratrole, 2-nitroanisole and 4-nitroanisole with CDs and establishes clearly that the aryl ring is positioned within the cavity.

α-CD and marginally higher in β-CD (compared to γ-CD) indicating that α-CD with its smaller cavity ensures a tighter fit to the guest. However the values are not too different between β- and γ-CDs, especially with 4-nitroanisole (a small linear molecule) reflecting that the relatively larger the cavities of β- and γ-CDs makes little difference in their binding. Mode of inclusion of (**1a**), (**2a**) and (**3a**) inside CD are presented in Scheme 3. For (**1a**) and (**2a**), only one kind of inclusion is likely as this is the least sterically hindered mode. However for (**3a**), complex formation can happen by two ways and reactivity from both the complexes is expected.

Three kinds of mechanistic pathways are proposed by van Riel et al. [11] to account for aromatic nucleophilic photosubstitution. (i) A direct displacement (S_N2Ar^*) route, in which the nucleophile adds onto the photoexcited substrate in its triplet state, yielding a σ-complex, that can either revert to the starting material or can give the substitution product, by expelling the leaving group. The reaction now, is HOMO-controlled [9] and the dominant interaction is between the HOMO of the substrate and the HOMO of the nucleophile. The nucleophile goes to the position *meta* to the nitro group and the regioselectivity is controlled by the size of the energy gap between the excited state nucleophile encounter complex and the ground state σ-complex, which is smaller in the *meta*-substitution (energy gap model). (ii) Mechanism involving electron-transfer from the nucleophile to the excited aromatic substrate ($S_N(ET)Ar^*$) [12]. This is followed by the coupling of the radical anion with the cationic or neutral radical formed from the nucleophile, forming a σ-complex. The position of attack is different, as the dominant orbital interaction is now between the LUMO of the aromatic substrate and the singly occupied HOMO of the nucleophile [9]. In this situation, replacement of substituents *para* to the nitro group takes place. Mutai and coworkers [13–16] have provided evidence for this kind of mechanism in their study of photo-Smiles rearrangement (an intramolecular aromatic nucleophilic photosubstitution reaction) in molecules of the type Ar–O–CH_2CH_2NHR. (iii) Electron transfer from the aromatic compound to an acceptor, followed by attack of the nucleophile on the aromatic radical cation ($S_{R+N}1Ar^*$ mechanism).

$$ArX^* \xrightarrow{Y^\ominus} [ArXY^\ominus] \xrightarrow{-X^\ominus} ArY \quad S_N2Ar^* \qquad \text{(i)}$$

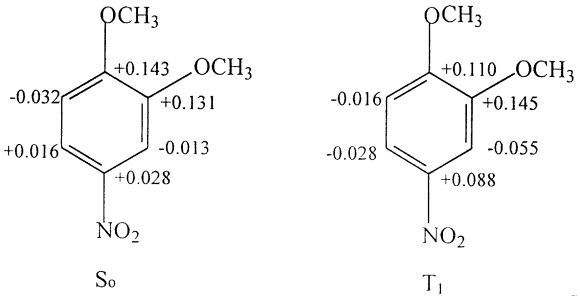
$$ArX^* \xrightarrow{Y^\ominus} [ArX^{*-o} + Y^o] \rightarrow [ArXY^\ominus] \xrightarrow{-X^\ominus} ArY \quad S_N(ET)Ar^* \qquad \text{(ii)}$$

$$ArX^* \xrightarrow{-e^-} [ArX]^{*+o} \xrightarrow{Y^\ominus} ArY \text{ or } Ar(-H)XY \quad S_{R+N}1Ar^* \qquad \text{(iii)}$$

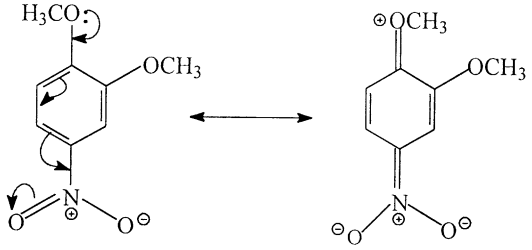
Regioselectivity also depends on the nucleophile and in the case of amine nucleophiles, on their ionisation potential. A pictorial representation of pathways (i) and (ii) is given in Scheme 2.

When (**1a**) is irradiated in solution, (**1b**) is formed exclusively. This is in accordance with the expected regioselectivity (*meta*-substitution) and S_N2Ar^* mechanism is operating under this situation. However, when α-, β- and γ-CD complexes of (**1a**) are irradiated in the presence of NaOH, a striking difference in regioselectivity is observed, in contrast to solution irradiation. Isomeric (**1c**), a product formed by the displacement of methoxy group *para*- to the nitro group, is obtained exclusively in CDs. We propose that upon CD encapsulation, a mechanistic changeover takes place and $S_N(ET)Ar^*$ pathway is now operating. This is attributed to an increase in the local concentration of the nucleophile, as at pH 11, it is likely that CD hydroxyl groups are ionized and their close proximity to the excited substrate facilitates electron transfer (Scheme 3). As a consequence of this mechanistic shift, the methoxy group which is *para*- to the nitro group is displaced.

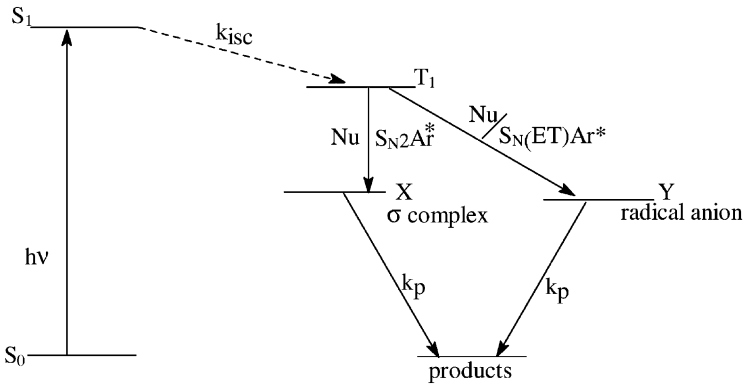
The observed results also find support in orbital considerations. In solution photolysis which is HOMO controlled and the operating mechanism is S_N2Ar^*, activation and *meta*-direction by nitro groups is well established [9,11,13] and accordingly (**1b**) is the exclusive product. Charge densities calculated [11] for the various positions of (**1a**) in the ground and lowest triplet states (CNDO/2 method) establishes the qualitative correlation with the observed reactivity. Positions with larger positive charge show higher reactivity.



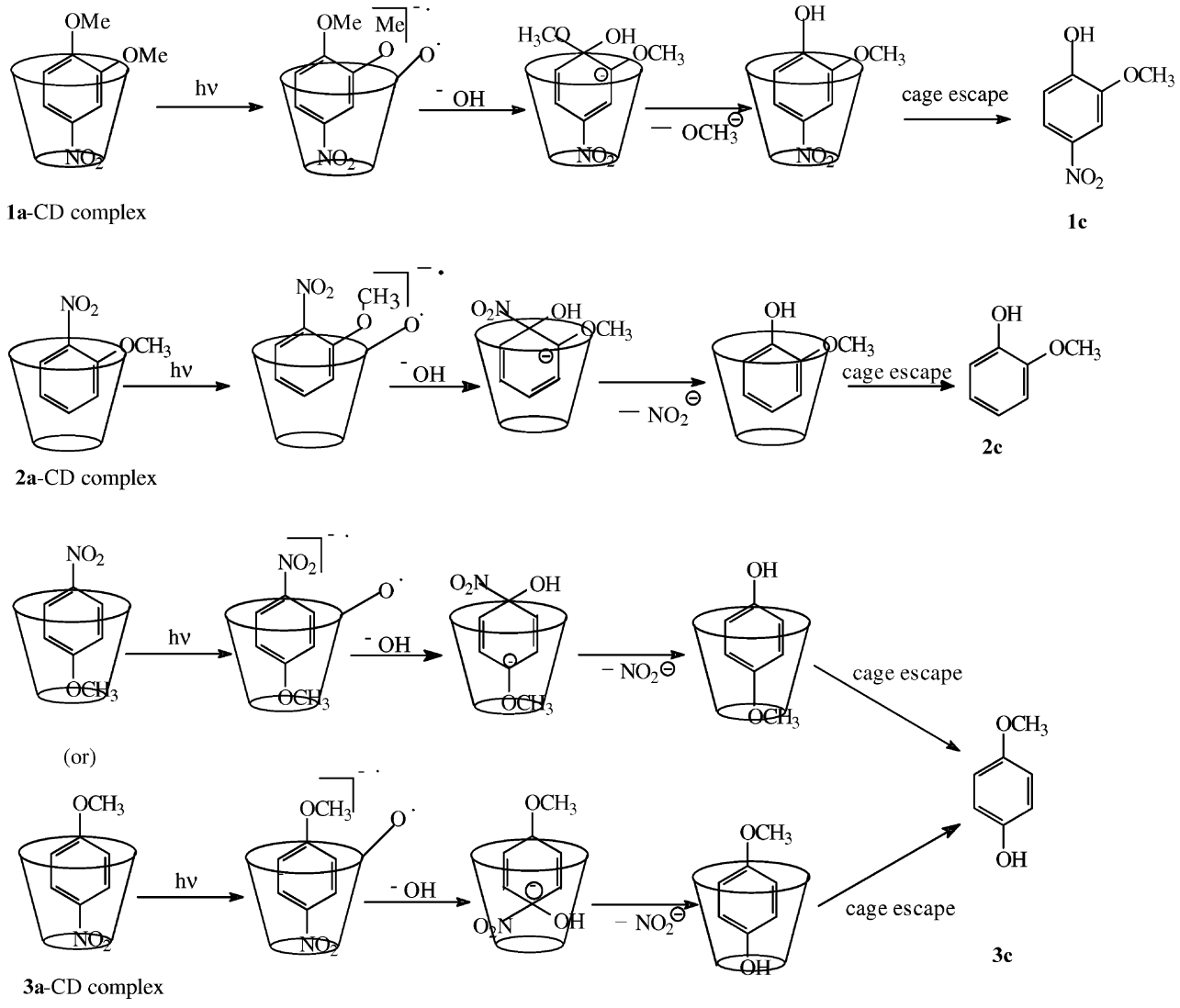
It is likely that a ground state monomeric interaction between *para*-methoxy and nitro groups as shown below, leaves the *para*-position less vulnerable for nucleophilic attack, despite its having a slightly higher positive value in S_0 state.



However, upon CD complexation of 4-nitroveratrole, the mechanistic changeover to $S_N(ET)Ar^*$ makes the reaction controlled now by the dominant interaction between the LUMO of the substrate and the HOMO of the nucleophile

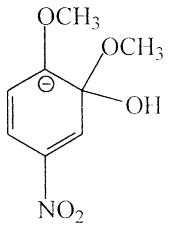


Scheme 2.

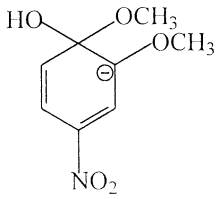


Scheme 3.

and a reactivity analogous to ground state reactivity prevails. The activating and *ortho-/para-* directing nature of the methoxy group (which dominates the deactivating and *meta* directing nitro group) controls the combination of 4-nitroveratrole radical anion with the hydroxyl radical to form a σ-complex. It is also likely that a simplistic explanation based on frontier orbitals may not be sufficient for $S_N(ET)Ar^*$ mechanism as, after electron transfer, energies, coefficients and charges will be very different from the ground state [17]. In this context, among other factors, the relative stabilities of the two possible intermediate σ-complexes (formed by the combination of the radical anion and the nucleophile radical) need to be considered.



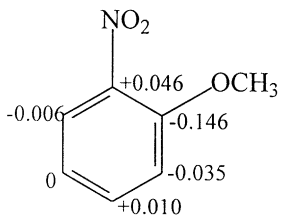
σ-Complex leading to (**1b**)
less stable



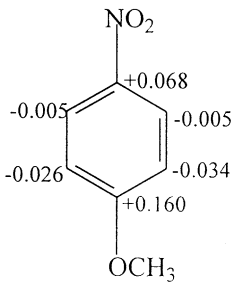
σ-Complex leading to (**1c**)
more stable

The complex leading to *para*-substitution is stabilized by resonance and hence is more favoured. Accordingly (**1c**) (in which *para*-methoxy is displaced) is the exclusive product. In addition, steric effects which accrue upon cyclodextrin complexation may also play a significant role. Upon inclusion into cyclodextrin cavity, not only the *para*-methoxy group of (**1a**) is more exposed (Scheme 3), there is also significant steric inhibition of ground state mesomeric interaction between the *para*-methoxy and nitro groups visualised earlier, thus leading to exclusive formation of (**1c**).

Studies on photohydroxylation are also extended to monomethoxynitroaromatics, i.e., 2-nitroanisole and 4-nitroanisole. Irradiation of (**2a**)/(**3a**) in solution results in a mixture of methoxy displaced (**2b**)/(**3b**) and nitro displaced (**2c**)/(**3c**) products. This is also in accordance with the charge densities for the various carbon atoms in the lowest triplet states of (**2a**) and (**3a**), calculated by CNDO/2 method [11].



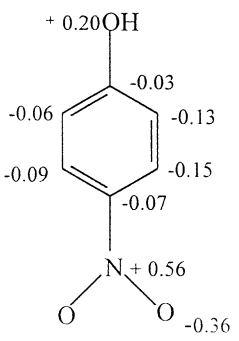
T_1



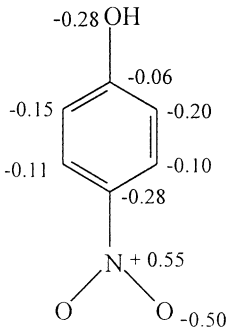
T_1

Carbon atoms bearing the substituents have the highest positive values and hence both NO_2 as well as methoxy groups can be displaced. Upon CD complexation, a significant increase in the rate of the reaction is observed and in addition, a dramatic regioselectivity is also observed. (**2c**) and (**3c**), in which the nitro group is displaced, are the exclusive products. Here also, as in the case of 4-nitroveratrole, upon CD complexation a change in mechanism from S_N2Ar^* to $S_N(ET)Ar^*$ is visualized. The subsequent LUMO (of substrate) control and the consequent methoxy activation (of reactivity) and *ortho-/para*-orientation (analogous to ground state reactivity) facilitates the formation of (**2c**) and (**3c**) exclusively.

It is also relevant to note here that in an electron-transfer mechanism, in which the electron-transfer step is followed by subsequent recombination of the substrate radical anion with the nucleophile radical, it is logical to expect a charge-controlled mechanism. The attack on the radical anion should take place at the most negative carbon atom of the aromatic ring. Based on Mulliken's analysis, Cantos et al. [17] have shown that the net negative charge on the carbon carrying nitro group (in *para*-nitrophenol, a very similar system) increases significantly on becoming the radical anion.



T_1



radical anion

By a similar reasoning, it is also likely in (**2a**) and (**3a**), the attack on the radical anion is most prolific at the carbon atom bearing the nitro group.

Thus CD complexation of methoxynitroaromatics, brings about a remarkable shift in mechanistic pathway (from a direct displacement path to one involving electron-transfer) and consequent alteration in regioselectivity. The percentage conversion is also higher in the presence CDs (Table 2). While photosubstitutions involving an electron-transfer pathway is commonly observed with amine nucleophiles of lower ionisation potentials, they are rare with oxygen nucleophiles as the ionization potential is relatively higher. To the best of our knowledge, the present study is one instance of photosubstitution with oxygen nucleophiles involving electron-transfer mechanism and CD complexation is primarily responsible for this. Thus the study presents an elegant demonstration of the usefulness of CDs as ideal hosts in exhibiting remarkable control on the photochemical reactivities of the included guests.

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