Photo-oxidation of phenylazonaphthol dyes and their reactivity analysis in the gas phase and adsorbed on cellulose fibers states using DFT and TD-DFT

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ABSTRACT

Reactivity of gaseous 1-arylazo-2-naphthol dyes and their complexes with cellulose, after adsorption on cellulose, towards singlet molecular oxygen, $^1O_2$, are investigated based on frontier molecular orbital theory. Results reveal that electrophilic reactions may occur predominately for the studied species, with the oxidizing agent $^1O_2$ as electrophile. The $-SO_3^-$ functionalized 1-arylazo-2-naphtol tautomers (soft nucleophiles) and their complexes with the cellulose are shown to be less reactive towards $^1O_2$ and under thermodynamic control; while the $-SO_3H$ functionalized 1-arylazo-2-naphtol tautomers (hard nucleuphiles) and their cellulose complexes are fairly reactive and under kinetic control. According to the frontier molecular orbital theory, the sites more vulnerable for $^1O_2$ attack (the atomic positions and double bounds) are similar for both azo dyes and their complexes with cellulose. Thermodynamic study reveals that the photo-oxidation reactions are exothermic and spontaneous, except for cycloaddition of hydrazone tautomers. TD-DFT calculations confirm the decolorization and color fading phenomenon during the photo-decomposition reaction.

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1. Introduction

Decolorization of colored textiles upon exposure to light is a well-known phenomenon and has been an active area of research for nearly 200 years [1]. The photodegradation is believed to proceed via a relatively complex mechanism. However, UV light-induced unimolecular decomposition and visible light-induced photo-oxidation, i.e. dye + UV-light → bleaching and dye + O$_2$ + Vis-light → bleaching, are among the most accepted pathways [2]. Actually, the photofading of commercial reactive dyes on cotton is due to both UV and visible lights, with the relative importance being determined by the dye type. As for the very popular azo/hydrazone dyes, degradation normally proceeds under visible light. It must be noted that presence of oxygen is essential for visible, but not UV, photo-degradation [1–3]. Electron transfer to oxygen is believed to be a key reaction in fading by sunlight.

Singlet molecular oxygen induced photofading is important when sensitizers (Senz) with high quantum yields for $^1O_2$ are present, which may be a particular dye type or impurities [4]:

$$Senz + light \rightarrow Senz^* \tag{1}$$

$$Senz^* + {}^3O_2 \rightarrow Senz + {}^1O_2 \tag{2}$$

In order to explain reactivity of the azo dyes in terms of molecular orbital theory, their chemical oxidation with $^1O_2$ has been simulated and analyzed using ab initio method. According to frontier orbital theory, chemical reactions between reagents A and B should take place preferentially in a direction which produces the most effective overlap between the HOMO of A and LUMO of B or vice versa. In the interaction of an electron-donor with an electron-acceptor, the orbital interaction between HOMO of the donor and LUMO of the acceptor governs the reaction. For electrophiles, HOMO electron density is closely related to the most reactive positions, while LUMO electron density determines the active sites against nucleophiles [5–8].

For the present study, 1-(arylazo)-2-naphtol and its sulfonated derivative in its two deprotonated ($-SO_3^-$) and protonated ($-SO_3H$) states, all in two tautomeric hydrazone and azo forms and the azo dyes adsorbed on cellulose, denoted as azo-dye/cellulose complexes, are considered. Fig. 1 shows the molecular structure, numbering scheme and hydrazone-azo tautomers of the dyes studied in this work. To study the azo-dye/cellulose complexes, a section of the cellulose I$_\beta$ crystalline structure (two cellulose chains consisting of three glucose units) is considered. To optimize the whole complex system, molecular plane of the azo dyes are set parallel to the cellulose plane with a suitable distance and direction.

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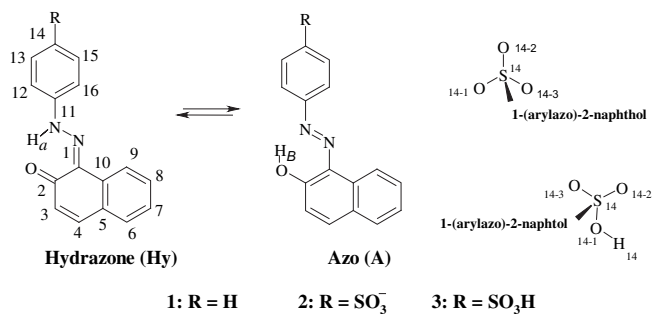E-mail address: nasserhadipour@gmail.com (N.L. Hadipour).

R
14
13   15
12   16
11
H$_a$ N   N
1
O   2   10   9
3   8
4   5   6   7
Hydrazone (Hy)

R

N
N
H$_B$
O

Azo (A)

O   14-2
S   14
14-1   O   O   14-3
1-(arylazo)-2-naphthol

14-3   O   S   14   O   14-2
O   14-1   H   14
1-(arylazo)-2-naphtol

1: R = H   2: R = SO$_3^-$ 3: R = SO$_3$H

Fig. 1. Molecular structure, numbering scheme and tautomers of 1-(arylazo)-2-naphtol dye, with different R substituents.

Details of the optimization procedure and characteristics of the optimized structures are reported elsewhere [9]. For brevity, the fully optimized structures of the azo-dye/cellulose complexes are presented in Fig. S1 of the Supplementary material.

2. Computational details

Global scalar properties (HOMO and LUMO orbital energies, E_{HOMO} and E_{LUMO}, chemical potential, μ, global hardness, η, and electrophilicity, ω) are calculated and evaluated for B3LYP/6-31G** optimized structures of the azo dyes and azo-dye/cellulose complexes. Molecular orbital calculations are carried out on the fully optimized azo dyes in the gas phase and adsorbed states (the azo-dye/cellulose complexes) within the same level of theory and basis set. Then the electrophilic frontier electron density, $f_r^{(E)}$, and the electrophilic reactivity of the double bonds, $S_{m,n}^{(E)}$, are calculated based on coefficients of the atomic orbitals. The thermodynamic quanitities ΔH_r^o, $T\Delta S_r^o$ and ΔG_r^o for photo-oxidation and photo-decomposition of the azo dyes with $^1O_2$ via the *ene* and *cycloaddition* reactions are calculated for the B3LYP/6-31G** optimized systems. Standard enthalpies of formation of the photo-decomposition products, ΔH_f^o, and sum of these values for each dye species, $\sum_i \Delta H_f^o(i)$, are calculated and analyzed [10].

Wavelengths and oscillator strengths, f, of the vertical transitions from the ground to the excited states of the photo-decomposed products are calculated using TD-B3LYP/6-31G** level of theory on the corresponding optimized geometries [10].

3. Results and discussion

In order to analyze the electrophilic and nucleophilic reactivities of the azo dyes in the gas phase and adsorbed states towards $^1O_2$, some important scalar quantities are calculated and investigated for B3LYP/6-31G** optimized structures. The calculated values of the molecular properties and their orbital definitions are listed in Table 1.

Energies of the HOMO and LUMO orbitals reveal the molecule's susceptibility towards electrophilic and nucleophilic attacks, respectively. Hard electrophiles have high LUMO energy while hard nucleophiles possess low HOMO energy [11]. Chemical potential, μ, serves as a measure for escaping tendency of an electron cloud and is considered as a global property of the ground state. It is found that polarizability and stability of interacting molecules are related to hardness [12]. Global hardness, η, can be defined as the resistance of a chemical species against charge transfer [13,14]. Liu and co-workers proposed electrophilicity index, ω, as a measure of energy lowering due to the electron flow between donor and acceptor [15]. Electrophilicity index, ω, encompasses both tendency of an electrophile to acquire an additional electronic charge driven by μ^2 (the square of chemical potential) and resistance of the system to electronic charge exchange with the environment, described by η [15,16]. The rate constants for reaction between a given dye and electrophile or nucleophile is calculated based on the relative difference between HOMO and LUMO energies [5].

All the calculated values reveal that $^1O_2$ is a good electrophile, while the azo dyes and their cellulose complexes exhibit nucleophilic properties. The $Hy - SO_3^-$ and $A - SO_3^-$ dyes, with the highest HOMO energies and lowest μ, η and ω values are the softest nucleophiles and hence, are oxidized easily. The $Hy - SO_3H$ and $A - SO_3H$ dyes are regarded as the hardest nucleophiles due to their low HOMO energies and high μ, η and ω values, and thus are hard to oxidize. Similar behaviors are observed for the corresponding azo-dye/cellulose complexes.

All azo dyes and their complexes have $\Delta E_{ele} < \Delta E_{nuc}$. Electrophilic reactions may occur predominately for the studied species and the oxidizing agent, $^1O_2$, acts as electrophile. Also, experimental results show a 10–30% contribution for the radical photo-degradation of 1-arylazo-2-naphthols on cotton with $^1O_2$ under visible light irradiation [17]. Therefore, in this research, only electrophilic reactions are studied. The $Hy - SO_3^-$ and $A - SO_3^-$ dyes and the $Hy - SO_3^-$/cellulose and $A - SO_3^-$/cellulose complexes have negative ΔE_{ele} values and large relative difference between the corresponding $E_{HOMO}(dye)$ and $E_{LUMO}(O_2)$, $|\Delta E_{ele}|$, values. Thus, they are oxidized very slowly, compared to other species.

Table 1
The scalar quantities including HOMO and LUMO orbital energies, E_{HOMO} and E_{LUMO}, chemical potential, μ, global hardness, η, electrophilicity, ω, and electrophilic and nucleophilic energy differences, ΔE_{ele} and ΔE_{nuc} (all in eV) obtained for the B3LYP/6-31G** optimized structures.

	Hy–H	Hy – SO$_3^-$	Hy–SO$_3$H	A–H	A – SO$_3^-$	A–SO$_3$H
E_{HOMO}	−5.530	−2.204	−6.005	−5.577	−2.232	−5.982
E_{LUMO}	−2.482	−0.368	−2.936	−2.410	−0.163	−2.936
$\mu = -(E_{LUMO} + E_{HOMO})/2$	4.006	1.286	4.470	3.994	1.198	4.459
$\eta = (E_{LUMO} - E_{HOMO})/2$	1.524	0.918	1.534	1.584	1.034	1.523
$\omega = \mu^2/2\eta$	5.265	0.901	6.513	5.035	0.694	6.528
$\Delta E_{ele} = E_{LUMO}(O_2) - E_{HOMO}(dye)$	0.653	−2.674	1.127	0.699	−2.645	1.105
$\Delta E_{nuc} = E_{LUMO}(dye) - E_{HOMO}(O_2)$	4.325	6.439	3.871	4.397	6.644	3.871

	$^1O_2$	Hy–H/ cellulose	Hy – SO$_3^-$/ cellulose	Hy–SO$_3$H/ cellulose	A–H/ cellulose	A – SO$_3^-$/ cellulose	A–SO$_3$H/ cellulose
E_{HOMO}	−6.807	−5.389	−3.481	−5.892	−5.418	−3.313	−5.836
E_{LUMO}	−4.878	−2.534	−0.748	−2.825	−2.216	−0.630	−2.763
μ	5.842	3.962	2.114	4.358	3.817	1.972	4.300
η	0.965	1.428	1.366	1.534	1.601	1.341	1.536
ω	17.683	5.496	1.636	6.190	4.550	1.450	6.017
ΔE_{ele}		0.512	−1.396	1.014	0.540	−1.565	0.958
ΔE_{nuc}		4.453	6.059	3.982	4.591	6.177	4.044