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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.

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]:

$$Senz + light \rightarrow Senz^* \quad (1)$$

$$Senz^* + {}^3O_2 \rightarrow Senz + {}^1O_2 \quad (2)$$

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_β 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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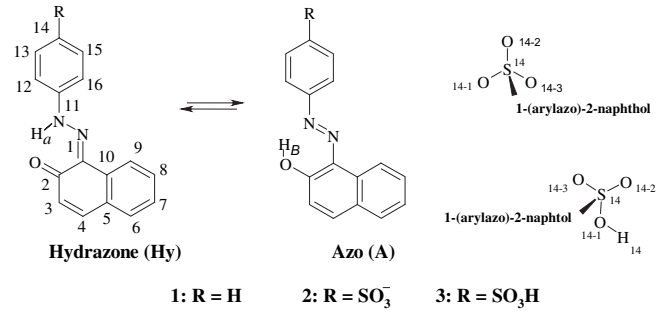

Fig. 1. Molecular structure, numbering scheme and tautomers of 1-(arylazo)-2-naphtol dye, with different R substituents.

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 photodegradation 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_3H	A–H	A $-$ SO_3^-	A–SO_3H
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_3H/ cellulose	A–H/ cellulose	A $-$ SO_3^-/ cellulose	A–SO_3H/ 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

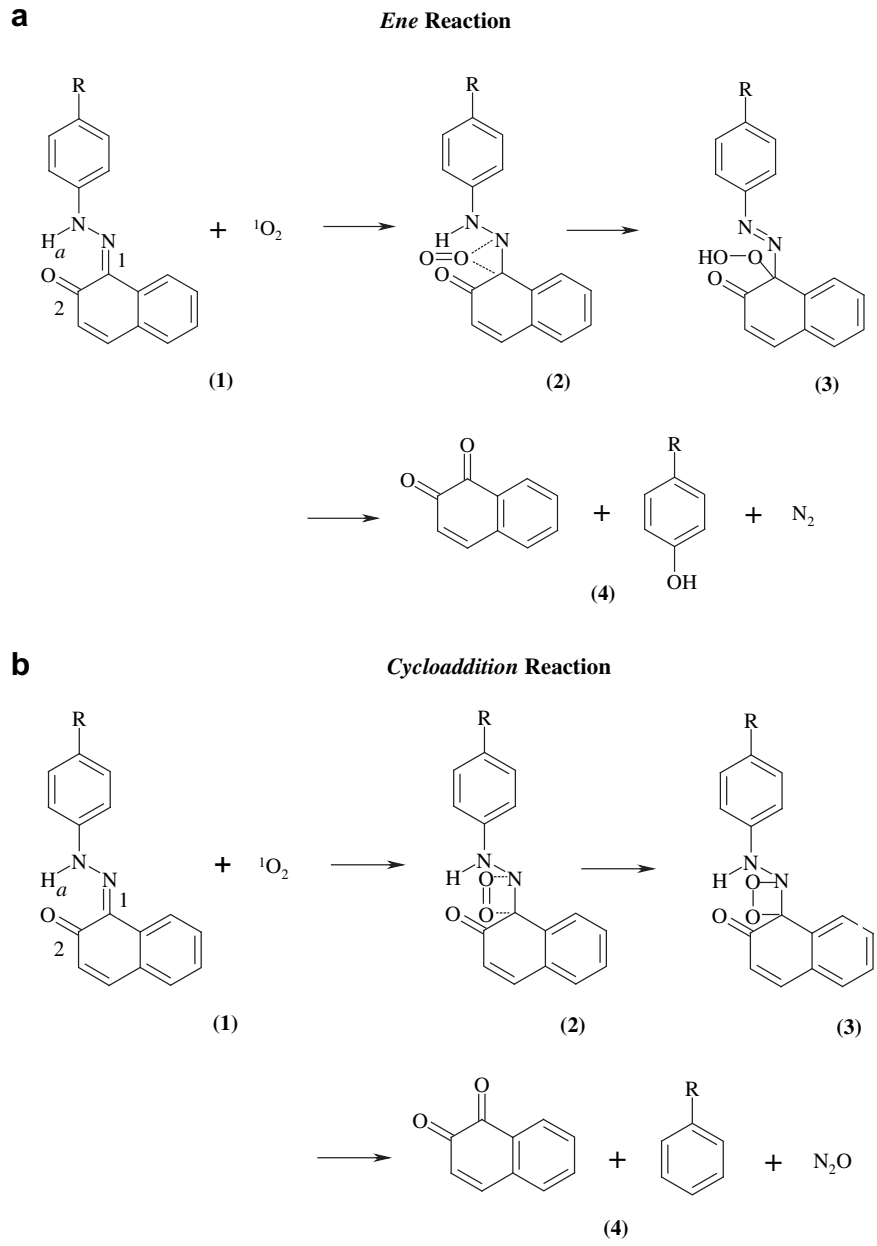

Fig. 2. (a) *Ene* ($C_1 = N_1$; H_a) and (b) [2 + 2] *cycloaddition* ($C_1 = N_1$) reactions of the hydrazone tautomers with $^1O_2$. In (a), the *ene* intermediate 2 is produced by $^1O_2$ addition to the $C_1 = N_1$ of the dye, and the species 3 is a hydroperoxide, and the species 4 are the final photo-decomposed products. In (b), the *cycloaddition* intermediate 2 is produced by parallel addition of $^1O_2$ to the $C_1 = N_1$ bond of the dye, and the 1,2-dioxetane 3 is formed via the [2 + 2] *cycloaddition*, and the photo-decomposed products 4 are formed from 1,2-dioxetane via the scission of the $C_1 = N_1$ bond.

In previous reports, the extent of solvation of the azo dyes in cellulose was assumed to lie between those in water and in the gaseous state; and reactivity of the tautomers in cellulose was approximated to that of the corresponding tautomers in the gas phase [18,19]. Based on experimental results and our calculations, the azo dyes bind to cellulose via the functional groups, such as hydroxyls present on the surface of cellulose [9,20–24]. This leads to some changes in reactivity of the azo dyes, which will be considered in this study.

The absolute value of ΔE_{ele} is found to be larger for each azo dye compared to its corresponding complex. This result reveals that in the gas phase, the azo dyes are more reactive towards $^1O_2$, compared to the azo-dye/cellulose complexes. Only a slight difference is detected between the reactivities of the two tautomers of the azo dyes. A similar reactivity trend is observed for the tautomers of the azo-dye/cellulose complexes.

According to frontier molecular orbital theory, the sites with the highest HOMO electron density are the most vulnerable to electrophilic attack. Electrophilic frontier electron density at the r atomic position, $f_r^{(E)}$, can be calculated as:

$$f_r^{(E)} = \sum_i \left(C_{ri}^{HOMO}\right)^2 \tag{3}$$

where C_{ri}^{HOMO} is the coefficients of atomic orbitals in the HOMO and i is the number of atomic orbitals [6,7,25,26]. Higher $f_r^{(E)}$ value indicates more reactivity of the atomic position to electrophilic attack. Electrophilic reactivity of all double bonds towards $^1O_2$ may

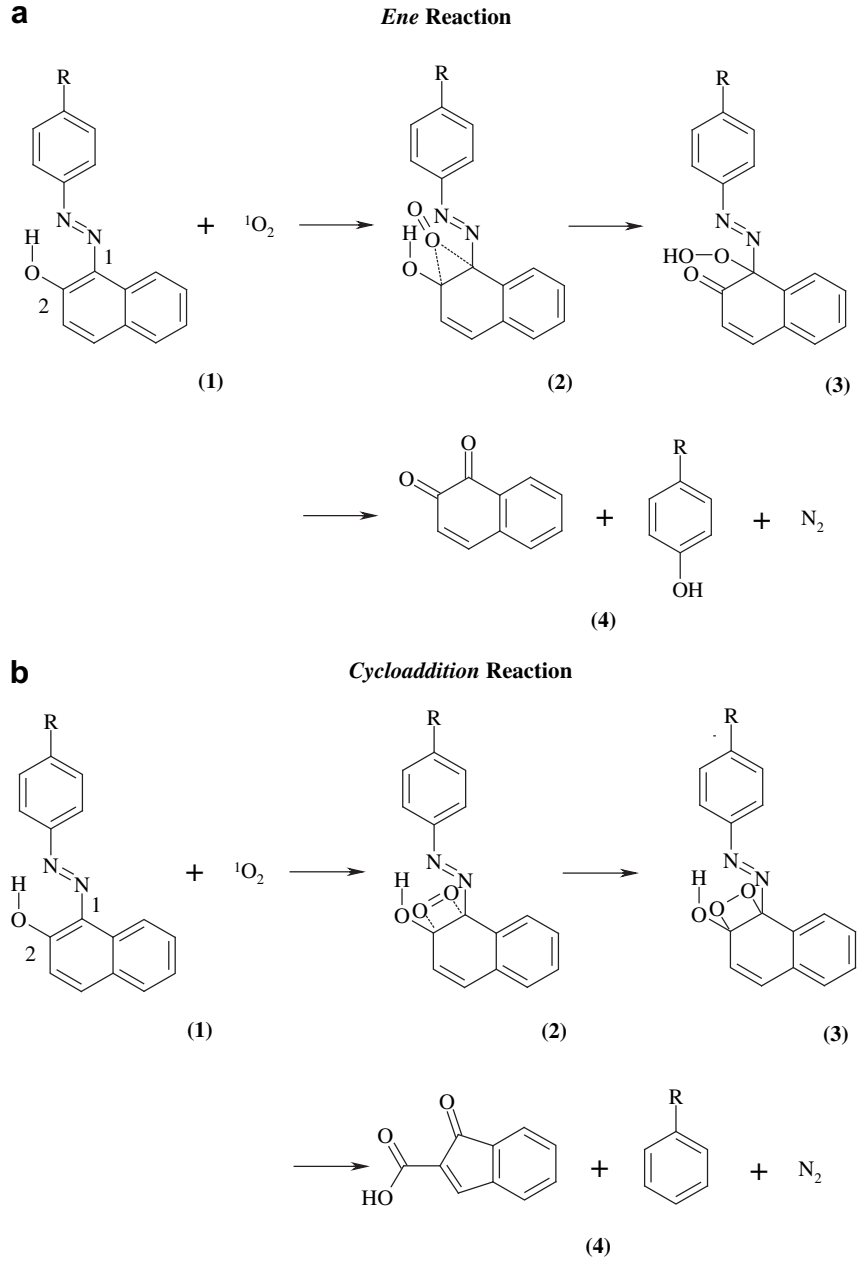

Fig. 3. (a) *Ene* ($C_1 = C_2$; H_β) and (b) [2 + 2] *cycloaddition* ($C_1 = C_2$) reactions of the azo tautomers with $^1O_2$. In (a), the *ene* intermediate 2 is produced by $^1O_2$ addition to the $C_1 = C_2$ of the dye, and the species 3 is a hydroperoxide, and the species 4 are the final photo-decomposed products. In (b), the *cycloaddition* intermediate 2 is produced by parallel addition of $^1O_2$ to the $C_1 = C_2$ bond of the dye, and the 1,2-dioxetane 3 is formed via the [2 + 2] *cycloaddition*, and the photo-decomposed products 4 are formed from 1,2-dioxetane via the scission of the $C_1 = C_2$ bond.

be described as the sum of $f_r^{(E)}$ at the two adjacent A_m and A_n atomic positions [18,19]:

$$S^{(E)} = \sum_{m,n} S_{m,n}^{(E)} = \sum_{m,n} \left\{ f_m^{(E)} + f_n^{(E)} \right\} \tag{4}$$

where the $S_{m,n}^{(E)}$ values are contribution of the specific $A_m = A_n$ double bond to the $S^{(E)}$ value. According to previous reports, there is a linear relationship between $\log(k_0)$ (where k_0 is the second-order rate constant) and $S_{m,n}^{(E)}$ [27].

Chemical reactions of organic compounds, such as hydroxylazo and heterocycles, and $^1O_2$ is shown to proceed via two different reaction modes producing (1) dioxetanes or carbonyl fragments via [2 + 2] addition (*dioxetane* reaction), and (2) allylic hydroperoxides via 1,3-addition (*ene* reaction) [27–30]. The reaction schemes for the *ene* and *cycloaddition* reactions of the dye tautomers are shown in Figs. 2 and 3. The highest $f_r^{(E)}$ and $S_{m,n}^{(E)}$ values for the azo dyes and azo-dye/cellulose complexes, calculated based on B3LYP/6-31G** method, are reported in Table 2. Some atomic positions with relatively large electron densities are also specified in this Table. Results reported in Table 2 show larger electron density on the atoms in the bridge (azo and hydrazone) groups such as C_1, N_1, O_2 and N_{11} in the Hy – H, A – H, Hy – SO_3H and A – SO_3H dyes and their complexes with cellulose. Therefore, oxygen molecules are attached to these atoms. In these dyes and their complexes, identical atomic positions and double bonds have the highest $f_r^{(E)}$ and $S_{m,n}^{(E)}$ values.

Due to their high electron density, the Hy – SO_3H and A – SO_3H dyes (hard nucleophiles) and their complexes with cellulose are

Table 2
The electrophilic frontier electron density at corresponding atomic positions, $f_r^{(E)}$, and double bonds, $S_{m,n}^{(E)}$, for the azo dyes and azo-dye/cellulose complexes obtained based on the B3LYP/6-31G** optimized structures.

$f_r^{(E)}$ or $S_{m,n}^{(E)}$	Hy–H	Hy – SO_3^-	Hy–SO_3H	Hy–H/cellulose	Hy – SO_3^-/cellulose	Hy–SO_3H/cellulose
C_1	0.105	0.0	0.096	0.106	0.019	0.093
N_1	0.013	0.0	0.023	0.011	0.0	0.0
C_2	0.014	0.0	0.012	0.015	0.002	0.013
O_2	0.067	0.0	0.063	0.068	0.008	0.063
C_{10}	0.018	0.0	0.028	0.017	0.0	0.032
C_{11}	0.026	0.0	0.013	0.027	0.010	0.012
N_{11}	0.154	0.0	0.157	0.150	0.013	0.154
O_{14-1}	–	0.236	0.006	–	0.198	0.006
O_{14-2}	–	0.247	0.003	–	0.237	0.003
O_{14-3}	–	0.237	0.004	–	0.187	0.004
S_{14}	–	0.0	0.002	–	0.001	0.002
$C_1 = N_1$	0.118	0.0	0.119	0.117	0.019	0.093
$C_2 = O_2$	0.081	0.0	0.075	0.083	0.010	0.075
$f_r^{(E)}$ or $S_{m,n}^{(E)}$	A–H	A – SO_3^-	A–SO_3H	A–H/cellulose	A – SO_3^-/cellulose	A–SO_3H/cellulose
C_1	0.118	0.0	0.118	0.117	0.0	0.118
N_1	0.002	0.0	0.0	0.004	0.0	0.0
C_2	0.053	0.0	0.049	0.055	0.0	0.050
O_2	0.065	0.0	0.061	0.064	0.0	0.062
C_{10}	0.004	0.0	0.008	0.003	0.0	0.007
C_{11}	0.020	0.0	0.010	0.021	0.0	0.012
N_{11}	0.082	0.0	0.091	0.079	0.0	0.088
O_{14-1}	–	0.237	0.004	–	0.239	0.003
O_{14-2}	–	0.246	0.002	–	0.245	0.002
O_{14-3}	–	0.238	0.003	–	0.210	0.003
S_{14}	–	0.0	0.001	–	0.001	0.001
$C_1 = C_2$	0.017	0.0	0.167	0.172	0.0	0.168
$N_1 = N_{11}$	0.084	0.0	0.091	0.082	0.0	0.089

fairly reactive species; so it can be predicted that they react quickly and irreversibly with $^1O_2$. The reaction is dictated by the kinetics of possible attacks and not the thermodynamics of possible products. Thus, the possible products of this photo-oxidation reaction are not necessarily the most stable ones. At equivalent positions where the Hy – H, A – H, Hy – SO_3H and A – SO_3Hdyes show the highest $f_r^{(E)}$ and $S_{m,n}^{(E)}$ values, the Hy – SO_3^- and A – SO_3^- dyes and their cellulose complexes exhibit the $f_r^{(E)}$ and $S_{m,n}^{(E)}$ values equal or near to zero. They are thus less reactive and this allows formation of more thermodynamic stable products. This is in accordance with the results obtained based on the $|\Delta E_{ele}|$ values. Therefore, the photo-oxidation of the Hy–SO_3H and A–SO_3H dyes with the –SO_3H electron-withdrawing functional group are under kinetic control and more are reactive than the Hy – SO_3^- and A – SO_3^- dyes with the –SO_3^- electron-donating functional group which undergo photo-oxidation reaction under thermodynamic control.

Hihara et al. reported that PM5 method may work well in treating the reaction behaviors of phenylazonaphthols with electron-withdrawing groups against $^1O_2$. However, the method appears to work poorly in treating those with electron-donating groups as their calculated values of rate constants obtained for these species are smaller than the corresponding experimental values [5]. This is in agreement with our above reasoning.

In thermodynamic studies, ΔH_r^o, $T\Delta S_r^o$ and ΔG_r^o are calculated for the B3LYP/6-31G** optimized structures in the **(1)** → **(3)** and **(3)** → **(4)** transformations (Table 3). The (azo ↔ hydrazone) tautomeric equilibrium constants, K_T, have been calculated and reported elsewhere [9,31,32]. The K_T values larger than 1 reveal that the hydrazone form is more stable than the azo form, and therefore, hydrazone tautomers are more important and effective forms in photo-oxidation reactions with $^1O_2$. Our results show that the considered **(1)** → **(3)** photo-oxidation reactions are exothermic and spontaneous with an exception for *cycloaddition* of hydrazone tautomers, which are endothermic and non-spontaneous. The result is in accordance with the experimental reports of Griffiths and Hawkins for photo-oxidation reactions of some hydrazone tautomers of phenylazonaphthols with $^1O_2$ [33]. All *ene* reactions have less negative entropy changes than the corresponding *cycloaddition* reactions.

The ΔH_r^o, $T\Delta S_r^o$ and ΔG_r^o thermodynamic values calculated for the **(3)** → **(4)** photo-decomposition reactions indicate that all reactions in this path are exothermic and spontaneous with

Table 3
The ΔH_r^o, $T\Delta S_r^o$ and ΔG_r^o (in kcal/mol) thermodynamic quantities calculated for the gas phase photo-oxidation of the azo dyes with $^1O_2$ and (a) *ene* and (b) *cycloaddition* mechanisms corresponding to the B3LYP/6-31G** optimized structures in the **(1)** → **(3)** and **(3)** → **(4)** transformations.

	Hy–H		Hy – SO_3^-		Hy–SO_3H		A–H		A – SO_3^-		A–SO_3H	
(1)→(3)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
ΔH_r^o	−20.3	9.9	−27.1	9.6	−22.9	5.5	−26.8	−16.5	−25.2	−19.5	−24.4	−14.8
$T\Delta S_r^o$	−8.9	−10.3	−10.0	−10.5	−10.2	−10.6	−10.0	−11.4	−9.4	−11.1	−10.2	−11.7
ΔG_r^o	−11.4	20.2	−17.1	20.1	−12.7	16.1	−16.8	−5.1	−15.8	−8.4	−14.2	−3.1
(3)→(4)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
ΔH_r^o	−104.7	−81.6	−92.3	−76.0	223.0	−77.3	−99.3	−121.8	−94.9	−113.2	222.8	−124.2
$T\Delta S_r^o$	22.3	24.1	23.6	24.5	22.6	24.5	23.4	25.4	22.9	25.2	22.5	24.2
ΔG_r^o	−127.0	−105.7	−115.9	−100.5	200.4	−101.8	−122.7	−127.3	−117.8	−138.4	200.3	−150.0

Table 4
The standard enthalpies of formation, ΔH_f^o, (in kcal/mol), maximum wavelengths (in nm) and oscillator strengths, *f*, of the vertical transition from ground to excited states of the photo-decomposition products of the azo dyes, respectively. Calculations are performed on the corresponding optimized geometries, obtained at the B3LYP/6-31G** and TD-B3LYP/6-31G** levels of theory.

		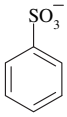	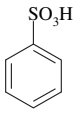	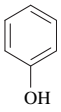	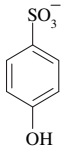	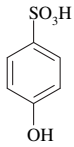	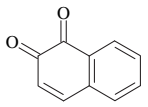	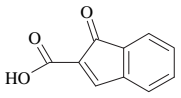
ΔH_f^o	25.2	−76.9	−36.1	−11.5	−113.3	252.2	−0.7	17.0
λ_{max}	168.4	242.2	209.2	174.4	232.8	222.3	397.9	400.0
f	0.56	0.08	0.10	0.33	0.14	0.22	0.05	0.04

Table 5
The sum of standard enthalpies of formation, $\sum_i \Delta H_f^o(i)$, (in kcal/mol) for the products of the azo dyes photo-decomposition via the (a) *ene* and (b) *cycloaddition* reactions, obtained for the B3LYP/6-31G** optimized structures.

Hy−H		Hy − SO_3^-		Hy−SO_3H		A−H		A − SO_3^-		A−SO_3H	
(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
−12.2	41.0	−114.0	−61.1	251.5	−20.3	−12.2	42.2	−114.0	−59.9	251.5	−19.1

positive entropy changes. However, there is an exception for *ene* photo-decomposition of the Hy − SO_3H and A − SO_3H dyes which are endothermic and non-spontaneous. Hence, it can be concluded that photo-decomposition of the Hy − SO_3H and A − SO_3H dyes to the expected products (Figs. 2a and 3a) is impossible. The calculated values of ΔH_r^o, $T\Delta S_r^o$ and ΔG_r^o thermodynamic quantities for the **(3)** → **(4)** *cycloaddition* transformation of hydrazone tautomers shows that this reaction is exothermic and spontaneous. However, their overall photo-decompositions are impossible since their corresponding **(1)** → **(3)** transformations are overwhelmingly non-spontaneous.

Due to our systematic limitations for complete vibrational analysis of the whole azo-dye/cellulose complex systems, it is not possible to obtain exact values of ΔG_r^o for the photo-oxidation reaction of the adsorbed azo dyes with $^1O_2$. However, our results disclose that the atomic positions and double bonds with the highest $f_r^{(E)}$ and $S_{m,n}^{(E)}$ values are similar for both the azo dyes and their complexes. Therefore, the sites more suitable for $^1O_2$ attack and the reaction mechanism is assumed to be the same for both isolated and adsorbed azo dyes.

In order to investigate the most stable photo-decomposition products, especially those obtained from soft nucleophiles (under thermodynamic control), one must consider all the possible positions for $^1O_2$ attack to double bonds and their reaction mechanism. For this purpose, the sum of standard formation enthalpies, $\sum_i \Delta H_f^o(i)$, needs to be calculated and compared for the products.

In the present study, the $\sum_i \Delta H_f^o(i)$ values are calculated for the products obtained from $^1O_2$ attack to double bonds with the highest HOMO electron density, $f_r^{(E)}$, only. The standard enthalpies of formation of photo-decomposition products, ΔH_f^o, and the sum of these values for each dye species, $\sum_i \Delta H_f^o(i)$ are listed in Tables 4 and 5, respectively. The *ene* photo-decomposition reactions of both azo and hydrazone tautomers are found to have equal $\sum_i \Delta H_f^o(i)$ values.

Products of the Hy − SO_3H and A − SO_3H photo-decomposition via the *ene* reaction are shown to have positive ΔH_f^o values, which is an evidence for the instability of phenol hydrogen sulfonate compound. This result is confirmed regarding their non-spontaneous reactions in the **(3)** → **(4)** transformation (Table 3). The Hy − SO_3^- and A − SO_3^- dyes produce more stable products via the *ene* reaction, as compared to those of the *cycloaddition* reaction. This result is in agreement with experimental data reported by Griffiths and Hawkins [33,34].

Calculation of the maximum wavelengths, λ_{max}, and oscillator strengths, *f*, for the vertical singlet → singlet transitions are carried out for the photo-decomposition products of the azo dyes using TD-B3LYP/6-31G** level of theory for the corresponding optimized geometries. The results of these calculations are reported in Table 4. The obtained results reveal that among the photo-decomposition products, only 1,2-naphthaquinone and 1-oxo-1*H*-indene-2-carboxylic acid (the bicyclic products) have maximum wavelengths of 400 nm in the visible region with oscillator strengths in the range of 0.04–0.05; while the azo dyes have wavelengths in the range of 420–540 nm with oscillator strengths approximately equal to 0.4–0.5 [9]. Thus, photo-decomposition with $^1O_2$ leads to color fading.

4. Conclusions

Based on the *ab initio* calculations at B3LYP/6-31G** level of theory, the reactivities of 1-(arylazo)-2-naphthol dyes and the azo-dye/cellulose complexes toward $^1O_2$ are analyzed in terms of frontier orbital theory. The results can be summarized in terms of an analysis of the relationship between the reactivity and chemical structure of the reactive azo dyes as follows:

The electrophilic reactions may occur predominately for the studied species (with $^1O_2$ as electrophile).

Based on the analysis of the global scalar quantities (E_{HOMO}, E_{LUMO}, μ, η and ω) calculated for the azo dyes, it can be concluded that the Hy − SO_3^- and A − SO_3^- dyes are soft nucleophiles, while the Hy − SO_3H and A − SO_3H dyes are hard nucleophiles. The Hy − SO_3H and A − SO_3H dyes and their complexes with the cellulose are reactive species. They quickly and irreversibly react with $^1O_2$. The Hy − SO_3^- and A − SO_3^- dyes and their cellulose complexes are less reactive and react under thermodynamic control.

The *ene* and *cycloaddition* photo-oxidation of the azo dyes are shown to be exothermic and spontaneous, with an exception for the *cycloaddition* of hydrazone tautomers which is endothermic and non-spontaneous.

All photo-decomposition reactions are exothermic and spontaneous with positive entropy changes, except for the *ene* photo-decompositions of the Hy − SO_3H and A − SO_3H dyes which are endothermic and non-spontaneous. The Hy − SO_3^- and A − SO_3^- dyes give more stable products via *ene* reaction, compared to the *cycloaddition* procedure.

Based on the TD-B3LYP calculations, the products of photo-decomposition are colorless and their formation leads to color fading in the reaction mixture.

Appendix. Supplementary material

The fully optimized structures of the azo-dye/cellulose complexes (Fig. S1). Supplementary material associated with this paper can be found, in the online version, at doi:10.1016/j.dyepig.2010.08.009.

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