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Reactivity of phenylazonaphthol sulfonates, their estimation by semiempirical molecular orbital PM5 method, and the relation between their reactivity and azo-hydrazone tautomerism

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Abstract

With respect to 4-phenylazo-1-naphthols and 1-phenylazo-2-naphthols, the azo-hydrazone tautomerism (AHT) of the undissociated and dissociated (UD&D) species for their *p*-sulfo derivatives (Orange I and Orange II) was analysed estimating their enthalpies of formation in both the gaseous phase and water using semiempirical molecular orbital (MO) (PM5 and COSMO) methods. The reactivities of these phenylazonaphthols against oxidizing agents including singlet molecular oxygen were examined using simple frontier orbital theory. The hydrazone tautomers (HT's) of the UD species of the two orange dyes had higher stability in water than the azo tautomers (AT's), while the two tautomers of the D species had similar stability. Both the UD&D species of the dyes resulted in AHT and furthermore both the tautomers of the dyes displayed an acid–base equilibrium. The assumption that the HT's had smaller pK_a values than the AT's explained some of the experimental results observed. Frontier orbital theory showed that the azo and hydrazone tautomers (A&HT's) for the UD and D species of two orange dyes as well as the A&HT's for phenylazonaphthols with several substituents had similar reactivity towards oxidants in terms of the interaction between HOMO and LUMO, although the positions of reaction changed in the tautomers used. The dissociation of hydroxyazo dyes and/or oxidants changed their mutual reactivity due to a rise in E_{HOMO} and E_{LUMO}, although the A&HT's for the D species of orange dyes had almost the same electronic structure as each other, irrespective of the different sites of ionization.

Keywords: Azo dye with sulfonate groups; Reactivity of azo and hydrazone tautomers; Molecular orbital method; Super-delocalizability oxidation; Photo-oxidation

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1. Introduction

Five decades after the first discussion of the azo-hydrazone equilibrium [1], Kuhn and Bär [2]

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confirmed the establishment of a mobile equilibrium between the two tautomers using firstly the *O*-methyl derivative as a model of the AT's. In the 1950′s, Burawoy et al. [3,4], Müller et al. [5], and Fischer and Frei [6] used *O*- and *N*-methyl derivatives to assign the absorption spectra of the A&HT's in their studies of AHT. Hydroxyazo dyes exhibit acid–base equilibria as well as AHT [7]. It has been reported that although the UD&D species of dyes displayed different oxidative reactions towards oxidizing agents (oxidants) [8–16], the AHT seems to be hidden by the acid–base equilibrium. Since the oxidants are involved in the acid–base equilibria and the reagent reactivity changes with dissociation, there may be many combinations of interactions between the UD&D species of dyes and oxidants. In the reaction with oxidants, it has not yet been resolved which species of dyes, nonionic, anionic or free radicals are involved in reaction scheme. From an experimental standpoint, the addition of an effective radical scavenger is essential; otherwise, related reactions become either radical controlled or diffusion controlled.

In the present study, hydrogen peroxide and hypochlorous acid as well as singlet molecular oxygen were examined as reagents. Even if ionic reactions are taken into consideration, the acid–base equilibrium of hydrogen peroxide ($pK_a = 11.75$) and hypochlorous acid ($pK_a = 8.50$) plays an important role. These two may exist as the UD&D species, respectively, (HX and X^-,) depending upon the pK_a of the oxidant and the pH of their aqueous environment.

Hydroxyazo dyes, on the other hand, exist as an AT and/or an HT depending upon their character and the solvent and both the tautomers display an acid–base equilibrium. Thus they may exist as four kinds of UD&D species for the A&HT's. In principle, there may be eight combinations of reaction between a given dye and an oxidant. In the present study, the reactivities of Acid Orange I and II were analysed in detail using quantum-mechanical theory. The values of pK_a reported for hydroxylazo dyes seem to be attributed to those of the hydroxyl groups even when they are believed to exist as HT's.

In the last decade, using a combination of high-resolution X-ray powder diffraction and the molecular modeling techniques including ab initio and semiempirical MO methods, crystal structure and electronic properties of organic solid colorants such as azo dyes [17–20], phthalocyanine [21,22], and triphenodioxazine [23,24] were examined. No application to dyes with sulfonate groups has been reported, since it may be impossible. As mentioned below, the potentiality of the semi-empirical PM5 MO method, which may be one of the few methods applicable to azo dyes with sulfonate groups, is discussed in this paper.

According to frontier orbital theory [25–27], on the other hand, only the interactions between HOMO and LUMO for a given dye and an oxidant can occur. Although the possible interactions between the various dye-oxidant combinations are numerous, the values of the second-order rate constants of reaction between Acid Orange I and II with hydrogen peroxide and hypochlorous acid [8,9,12] may be predicted using the MO method taking the possible combinations into account.

The AHT of phenylazonaphthols was examined in detail [28] in both the gaseous phase and water to show that the AHT was determined by solvation. Sulfonic acid groups at the *o*-position relative to the azo groups have shown to have an unusual solvation effect on the dye so as to promote AT's in water.

In the present paper, the AHT of the UD&D species for Acid Orange I and Acid Orange II is discussed on the basis of data reported so far [28] as well as the results of PM5 and COSMO calculations. The reactivity of the A&HT's of Acid Orange I and II, towards oxidants, as well as that of 4-phenylazo-1-naphthols and 1-phenylazo-2-naphthols against singlet molecular oxygen, is also analysed using frontier orbital theory to prove a small difference in the reactivity between the A&HT's and a large one in the reactivity between each tautomer and the *N*- or *O*-methyl derivative. As a result of both the present and previous studies [28], the chemical structures of hydroxyazo dyes, drawn as HT's in the Colour Index, should be re-examined, since they may be erroneous or meaningless due to the solvent-dependence of AHT.

2. Experimental

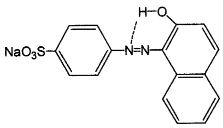
2.1. MO calculation

Semi-empirical MO calculations based on PM5 Hamiltonian were carried out using CAChe Work System, MOPAC 2002 (Fujitsu Ltd.) [29] on a Mackintosh G4 computer to estimate the enthalpy of formation, H_f (at 25 °C) in both the gaseous phase and water. In the solvation modeling, the COSMO method in MOPAC 2002 was also used.

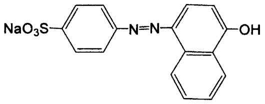
2.2. Dyes used

The dyes used are shown below as the C.I. Generic Name, the Constitution Number, if available, and the abbreviations in parentheses are given.

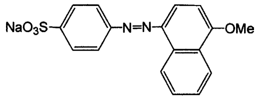
1. C.I. Acid Orange 7, C.I. 15510 (Orange II)



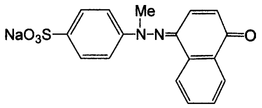
2. C.I. Acid Orange 20, C.I. 14600 (Orange I)



3. *O*-Methyl derivative of C.I. Acid Orange 20 (*O*-Me-Orange I)



4. *N*-Methyl derivative of C.I. Acid Orange 20 (*N*-Me-Orange I)



The other dyes used were described by the chemical nomenclature and by C.I. Generic Names, if available.

3. Results and discussion

3.1. AHT of UD&D species of hydroxyazo dyes

Interrelation between the acid–base equilibrium and the AHT of hydroxyazo dyes has not yet been explained clearly. It has been recognized [8–12,14,15] that the reactivity of hydroxyazo dyes changes drastically by the dissociation of hydroxyl groups, irrespective of the fact that these dyes exist predominantly as HT's in an aqueous solution, which contain no dissociable hydroxyl groups. In the present study, the authors try to explain how MO theory can solve these problems and can illustrate the acid–base equilibrium and the AHT as well as its interrelation between them. Before discussing the reactivity of these dyes with oxidizing agents, the AHT for the UD&D species of Orange I and II was analyzed using the semi-empirical MO methods. The enthalpies of formation (H_f) in both the gaseous phase and water for various species of Orange I and II and the *N*- and *O*-methyl derivatives of Orange I, calculated using MO methods, are listed in Tables 1 and 2.

In this work, assuming that the contribution of the entropy term to the Gibbs free energy change by AHT or solvation is small compared with the enthalpy term, and is then cancelled between the tautomers, the following equation was used to discuss AHT as in the previous paper [28]:

$$\log K_T \cong -\Delta H_T/2.303RT \cong -\Delta H_T/1.364 \qquad (1)$$

where ΔH_T (kcal mol^{-1}) denotes the difference in the standard enthalpies of two tautomers and K_T (–), the tautomeric equilibrium constants.

3.1.1. AHT of UD species

The AHT comprises quantum-mechanical proton tunneling across a low barrier in a double well between neighboring nitrogen and oxygen atoms, accompanied by electron transfer or a shift of a double bond [30]. Although the two tautomers can be observed by electronic spectroscopy, they can be observed neither by NMR nor vibronic spectroscopy since the equilibrium between two tautomers is too rapid to observe [31–37].

In the field of heterocyclic chemistry, the general energetic principles of tautomeric equilibrium

Table 1
Enthalpy of formation, H_f (kcal mol^{-1}), HOMO and LUMO energies, E_{HOMO} and E_{LUMO} (eV), electron density of HOMO and LUMO, d_{HOMO} and d_{LUMO}, at given atoms for Orange I and II in the gas phase, estimated by semiempirical molecular orbital PM5 method[a]

		Orange I						Orange II			
		AT	HT	O^--anion	N^--anion	O-Me	N-Me	AT	HT	O^--anion	N^--anion
M.W.		328.342		327.334		342.369		328.342		327.334	
H_f		−53.394	−55.170	−124.727	−124.726	−46.003	−48.234	−53.933	−56.355	−113.395	−118.225
E_{HOMO}		−8.729	−9.276	−4.962	−4.962	−8.704	−9.221	−8.942	−9.014	−4.720	−4.838
E_{LUMO}		−1.750	−1.844	1.215	1.215	−1.676	−1.584	−1.885	−1.943	1.394	1.499
d_{HOMO}	C1	0.212	0.110	0.227	0.227	0.212	0.163	0.223	0.162	0.279	0.276
	N_α	0.005	0.089	0.018	0.018	0.005	0.031	0.002	0.031	0.011	0.010
	N_β	0.071	0.284	0.238	0.238	0.071	0.247	0.083	0.243	0.223	0.226
d_{LUMO}	C1	0.031	0.092	0.029	0.029	0.028	0.058	0.016	0.059	0.009	0.010
	N_α	0.198	0.172	0.191	0.191	0.200	0.221	0.215	0.227	0.090	0.100
	N_β	0.174	0.035	0.018	0.018	0.172	0.038	0.168	0.041	0.011	0.012
	C_i	0.104/C2	0.139C2	0.138/C13	0.138/C13	0.106/C2	0.139/C2[b]	0.118/C2	0.140/C2	0.107/C13	0.115/C13

[a] In order to list the properties of two dyes in the same table, the numbering of carbon atoms is changed from that of chemical nomenclature. C1 is the coupling position by azo groups in naphthalene nucleus, C2 is the neighbouring (clockwise) atom of C1 atom, and C13 is the carbon atom bound with azo groups in the diazo component. N_α is the nitrogen atom of azo groups bound with naphthalene nucleus.

[b] d_{LUMO}, 0.106/C4.

Table 2
Enthalpy of formation, H_f (kcal mol^{-1}), HOMO and LUMO energies, E_{HOMO} and E_{LUMO} (eV), electron density of HOMO and LUMO, d_{HOMO} and d_{LUMO}, at given atoms for Orange I and II in water, estimated by semiempirical molecular orbital (PM5 and COSMO) method[a]

		Orange I						Orange II			
		AT[b]	HT[c]	O^--anion[d]	N^--anion	O-Me[e]		AT[f]	HT[g]	O^--anion	N^--anion[h]
M.W.		328.342		327.334		342.369		328.342		327.334	
H_f		−101.826	−107.316	−212.161	−213.743	−88.250	−100.198	−103.681	−104.080	−217.698	−216.318
E_{HOMO}		−8.882	−9.184	−8.480	−8.477	−8.856	−9.274	−9.172	−9.213	−8.683	−8.643
E_{LUMO}		−1.875	−2.189	−2.003	−1.981	−2.075	−1.981	−2.202	−2.196	−1.898	−1.945
d_{HOMO}	C1	0.226	0.128	0.255	0.227	0.223	0.163	0.226	0.192	0.256	0.266
	N_α	0.001	0.071	0.000	0.018	0.002	0.031	0.002	0.015	0.011	0.002
	N_β	0.081	0.268	0.111	0.238	0.083	0.247	0.083	0.207	0.162	0.128
d_{LUMO}	C1	0.009	0.067	0.000	0.029	0.015	0.058	0.016	0.060	0.001	0.000
	N_α	0.272	0.198	0.002	0.191	0.209	0.221	0.224	0.246	0.213	0.156
	N_β	0.139	0.023	0.001	0.018	0.161	0.038	0.147	0.041	0.085	0.080
	C_i	0.094/C2	0.143/C2	0.100/C16	0.138/C13	0.113/C2	0.139/C2	0.106/C2	0.158/C2	0.107/C13	0.087/C13

[a] See Table 1 on the numbering of atoms.

[b] d_{HOMO} 0.100/C3; 0.116/C4; 0.107/C9.

[c] d_{LUMO} 0.143/C2; 0.176/C4.

[d] d_{HOMO} 0.140/C3.

[e] d_{LUMO} 0.106/C4.

[f] d_{HOMO} 0.108/C6; 0.103/C7; 0.133/C9.

[g] d_{HOMO} 0.101/C7; d_{LUMO} 0.114/C4.

[h] d_{HOMO} 0.107/C7.

have been established [38–40]: Tautomerism occurs when two isomers have the same atomic composition and exist in mobile equilibrium with each other. In the energy barrier separating two tautomers, there is no fixed limit; they may be regarded as tautomers with $\Delta G < 25$ kcal mol^{-1}.

The values of H_f in Tables 1 and 2 show that the UD species of Orange I may exist predominantly as HT's in water, while those of Orange II as a mixture of the A&HT's, although the population of HT's is larger than that of AT's. The energy differences between HT's and AT's in H_f were, respectively, only 0.4 kcal mol^{-1} for Orange I and 5.5 kcal mol^{-1} for Orange II. (According to Stewart [29], the PM5 method improved accuracy up to four times greater than PM3 and AM1; the PM5 method calculates the values of H_f in the gaseous phase at 25 °C and the PM5/COSMO method in water.) This may indicate the existence of 7% of AT's for Orange I in terms of population ratio. The HT's of the two dyes have higher stability than the AT's as known [28]. The general principles of heterocyclic tautomerism hold well for the AHT of both dyes.

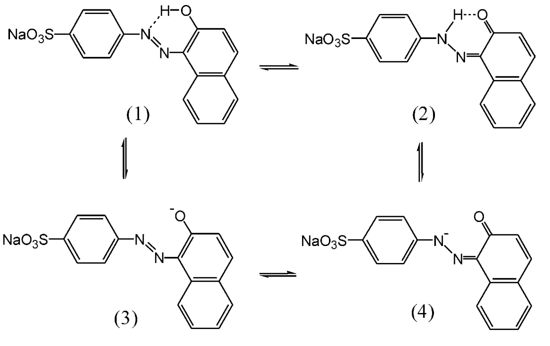
3.1.2. AHT of D species

The UD species of Orange I exists almost as HT, with those of Orange II as HT. In spite of the fact that both dyes were found to exhibit acid–base equilibrium, the existence and properties of their D species seem vague. When no AT's exist, no dissociation of hydroxyl groups should be observed. In spite of the absence of hydroxyl groups, the UD species of HT's have been considered to exhibit the acid–base equilibrium of hydroxyl groups. Griffiths [41], Bredereck and Schumacher [13–16], Oakes et al. [9–12], and Fedorov and Sokolovskii [42] explained this by assuming that the A&HT's of the D species are undistinguishable from each other; they called it the 'common anion'.

In order to confirm the existence or stability of the D species for both the A&HT's of the two dyes and to analyse how the MO theory exhibits these situations, the values of H_f in both the gaseous phase and water were estimated. The results of the MO calculation for the D species are also listed in Tables 1 and 2. In the gaseous phase, the values of H_f, orbital energies and electron densities in the various positions in HOMO and LUMO were almost identical for both tautomers of the D species of Orange I. Small differences in both electron densities and in the values of H_f were found between the tautomers of the D species of Orange II. Despite the different anionic sites in their molecule, the similarity of the tautomers of the D species may be well described by the results of MO calculation for both dyes. The similar (not the same) electronic structures of both the tautomers for the D species may show the indistinguishability of electronic spectra in the UV and visible regions, implying a common anion. (On the contrary, if both the HOMO levels correspond to the different electronic states of a molecule, the HOMO levels of two tautomers of the D species for Orange I may be regarded to be degenerated from each other. In this case even if both the tautomers are different isomers with similar electronic states but different anionic sites, the tautomers in very rapid dynamic equilibrium.) This situation may be explained by the assumption mentioned above [9–16]. Intramolecular anion transfer as well as a shift of double bond may occur quite rapidly via two kinds of intramolecular electron transfer to repeat the mutual generation of two kinds of anions.

In water, on the other hand, the MO calculation of the D species in water may throw new light on our knowledge of this phenomenon. The results in Table 2 differentiate the D species of AT's from those of the HT's. Insofar as they possess different values of H_f irrespective of the common large enthalpy decrease caused by ionization. The differences in H_f for the D species are within the same range of differences for the UD species. Since the values of H_f calculated might contain some errors, the AHT and the acid–base equilibrium were phenomenologically analysed. The D species of the HT's of Orange I exist in larger population than those of AT's, although the population of AT's increases by the deprotonation. The AHT and the acid–base equilibrium for Orange I may be illustrated as shown in Scheme 1, although it is drawn as those for Orange II.

In the case of Orange II, the behaviour seems more complex. The population ratio of AT/HT



Scheme 1. Azo-hydrazone tautomerism of UD species [(1)⇋(2)] and of D species [(3)⇋(4)] and acid–base equilibria of ATs [(1)⇋(3)] and of HTs [(2)⇋(4)] for Orange II.

for the UD species is 10^{-4}, while that for the D species is 10.3, the predominant species being AT's. When the HT's of Orange II dissociate via deprotonation of the -NH-N = groups, they generate the D species of HT's and at the same time the D species of AT's via AHT. In aqueous solution, the A&HT's of the UD species exist at a definite population ratio, while the UD and D species exist depending upon pK_a and the pH of the solution. The A&HT's of the D species exist at another definite population ratio. Since the four kinds of the UD and D species for the A&HT's exist depending upon the population ratio given by the difference in H_f, the compositions of the solution are very complex, if they could be identified. When considering the concentrations in equilibrium of the species, the equilibrium between the UD species of HT's and the D species of AT's holds. From the viewpoint of mechanism, there appears to be a two-step AHT. The AHT and the acid–base equilibrium for Orange II may be also described by Scheme 1 as that of Orange I.

3.1.3. Interrelation between AHT and acid–base equilibrium in water

MO calculation indicated that some reactive hydroxyazo dyes having *o*-sulfophenylazo groups may exist as AT's in water [28], although this speculation is not agreement with the result reported so far. Bredereck and Schumacher [13–16] investigated properties such as light fastness and reactivity towards hydrogen peroxide and hypochlorite for a series of derivatives of C.I. Reactive Red 227, but they seemed to recognize no existence of AT's.

The present authors propose the following interpretation of the multiple AHT. They explain it by introducing the following hypotheses:

1. Dissociation of the -NH-N = groups in the HT's results in a generation of an -N$^-$-N = anion (it should be observed when HT's exist);
2. The dissociation constants of the -NH-N = groups are larger than those of hydroxyl groups in the same hydroxyazo dyes. (One must observe an acid–base equilibrium of HT's; Many values of pK_a reported for hydroxyazo dyes should be the pK_a of the NH-N = group.)

These assumptions seem to be supported by some indirect proof: 1-(2′-Sulfophenylazo)-2-naphthol-6-sulfonate was reported to exist as HT in water and in DMSO–water solution [10]. In the present MO calculation, however, the AT of this compound had a higher stability than the HT in water and the differences in H_f between them were so small that two tautomers co-existed. A pronounced shift from HT to AT occurs by the addition of organic solvent in DMSO–water mixtures [43]. (This fact also applied to 1-(*p*-methoxyphenylazo)-2-naphthol [10].) There may be a fundamental problem on the assignment of two tautomers by spectral measurements. The findings, of MO calculation that the stability of the AT's of the *o*-sulfo compounds in both the gaseous phase and water is higher than that of the HT's, may be supported by an indirect experimental proof: the value of pK_a for this dye deviated considerably from the relationship between pK_a and NMR shift for the other dyes used [10].

Moreover, the hypotheses seem to be consistent with the NMR observations on pyrazolinyl azo dyes by Bell and Mazzola [44] and on phenylazonaphthols by Mazzola et al. [45,46]. (These workers consider that the observed NMR line broadening is due to slow proton transfer between -NH-N = and water.) The UD species of these dyes exist predominantly as HT's in aqueous solution. From acid–base equilibrium, the values of pK_a for the dissociation of the amino proton of an -NH-N = group should be determined. With an increase in pH, the UD species of AT's may be observed by NMR spectroscopy. (There are some observations of the AT's with an increase in pH [45]. This fact may be explainable only in terms of the above hypothesis.) The D species may exist as AT's in alkaline solution. Similar AHT and acid–base equilibrium of their UD and D species have been explained also by some workers [32,42,44–46], although they have not mentioned all of this behaviour, systematically.

3.2. Kinetic equation of the reaction of hydoxyazo dyes with oxidants

Before discussing the reactions of azo dyes with oxidants using MO theory, the experimental data of the reactions so far reported [8,9,12,47,48] are analysed. Assuming that only either one of tautomers of dye exists or the two tautomers have the same reactivity as each other in the dye–oxidant system, the kinetic equation of the second-order reactions between each species of dyes and oxidants, whose rate constants are described by k_i's ($\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$), may be written as follows:

$$-\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = k_1[\mathrm{DH}][\mathrm{XH}] + k_2[\mathrm{DH}][\mathrm{X}^-] + k_3 \times [\mathrm{D}^-][\mathrm{XH}] + k_4[\mathrm{D}^-][\mathrm{X}^-] \qquad (2)$$

where [D] is the total concentration of dye, whose UD species is denoted by DH and D species by D^-. XH and X^- denote the UD and D species of oxidant, respectively. If the values of pK_a for dye and oxidant are known, the concentrations of each species can be calculated from the total concentrations of dye and oxidant. However, no number of the rate parameters can be reduced and all the four parameters must be experimentally determined.

Oakes et al. [9] and the Lion Corporation group [47,48] found that the apparent rates of decomposition for Orange I and II by oxidants such as hypochlorous acid and hydrogen peroxide in weakly to strongly alkaline solution, exhibited a maximum at the pH of the midpoint of pK_a for both the dye and oxidant used and approached zero sufficiently, both above and below the midpoint. They concluded from the latter fact that the values of k_1 and k_4 were negligible, compared with the values of k_2 and/or k_3. Due to the symmetrical behaviour of the reactions above and below the midpoint of pH, however, no one can determine the values of k_2 and/or k_3 without introducing further preconditions.

In Table 3, the second-order rate constants of reaction with bleaching agents for Orange I, II and their *N*- and *O*-methyl derivatives [8,9,12,47,48] are summarized together with the preconditions necessary to determine their values. Although experiments simplify the complexity in Eq. (2), no essential reaction picture could be obtained. As mentioned below, theoretical treatments are more complex than Eq. (2) and need to be proved by experiments. No one has completely elucidated these problems so far. Since Eq. (2) takes into account no contribution of radical mechanisms, as reported recently [49], there may be inevitable limits in the theoretical and experimental investigations on the reaction of azo dyes with bleaching agents.

3.3. Reactivity of model azo dyes against oxidizing agents, estimated by MO method

In order to examine how the reactivity of azo dyes can be explained in terms of MO theory, the chemical reactions of model azo dyes against oxidants are analysed using the PM5 method. According to frontier orbital theory [25–27], chemical reactions between reagents A and B should take place preferentially at the position and in the direction in the space where the overlap between the HOMO of A and the LUMO of B and the overlap between the HOMO of B and the LUMO of A or mutual overlaps of frontier orbitals are most effective. In the interaction of an electron donor with an electron acceptor, the orbital interaction between the HOMO of the donor and the LUMO of the acceptor governs the reaction between A and B. The electron densities in the HOMO have a good correlation with the most reactive positions against electrophiles, while those in the LUMO against nucleophiles.

Fukui et al. [25] initially developed the frontier orbital theory using Hückel MO method and derived the superdelocalizability as follows:

Table 3
Rate constants of reaction, k_i (mol^{-1} dm^3 s^{-1}) (cf. Eq. (2)) with bleaching agents for Orange I, II and their *N*-Methyl and *O*-Methyl derivatives at 25 °C, which were determined under the preconditions described[a]

	Hydrogen peroxide			Hypochlorous acid		
	k_2: [DH][HO_2^-]	k_3: [D^-][H_2O_2]	k_1: [DH][HClO]	k_2: [DH][ClO^-]	k_3: [D^-][HClO]	$t_{1/2}$ (s) [8]
Precondition	$k_1 = k_3 = k_4 = 0$	$k_1 = k_2 = k_4 = 0$	$k_2 = k_3 = k_4 = 0$	$k_1 = k_3 = k_4 = 0$	$k_1 = k_2 = k_4 = 0$	
Orange I	0.3 [9]	2.0×10^{-4} [9]		9.5×10^3 [12]	1.1×10^5 [12]	
Orange I [47]	0.49	1.7×10^{-4}		3.5×10^4	2.8×10^5	
N-Me-Orange I	3.2×10^{-2} [9]	–		5×10^{-2} [12]		4.2×10^2
O-Me-Orange I	–		$6 <$ [9]			5.4×10^3
Orange II	4.5×10^{-2} [9]				1.3×10^5 [12]	
Orange II [47]	0.12	3.7×10^{-2}		45	2.5×10^5	

[a] p*K*a = 8.2 for Orange I and 11.4 for Orange II, p*K*a = 11.75 for H_2O_2 and 7.5 for HClO.

$$S^{(E)}(x) = 2\sum_{i}^{OCC} \frac{C_i(x)^2}{\alpha - E_i}(-\beta) \tag{3}$$

$$S^{(N)}(x) = 2\sum_{i}^{UNOCC} \frac{C_i(x)^2}{E_i - \alpha}(-\beta) \tag{4}$$

Here, $S^{(E)}(x)$ and $S^{(N)}(x)$ are, respectively, the electrophilic and nucleophilic superdelocalizability at point *x*; α and β are, respectively, Coulomb and resonance integrals given by the Hückel MO method for a planar-conjugated hydrocarbon molecule. The latter is multiplied to make it dimensionless. $C_i(x)$ denotes coefficient of the *i*th orbital at position x and E_i the energy of the *i*th orbital in eV. OCC and UNOCC mean that the summation is made, respectively, over all the occupied and unoccupied orbitals. Fukui et al. [25] showed that $S^{(E)}(x)$ and $S^{(N)}(x)$ can be approximated by only the contribution of, respectively, HOMO and LUMO as follows:

$$S'^{(E)}(x) \approx 2\frac{C_{HOMO}(x)^2}{\alpha - E_{HOMO}}(-\beta) \tag{5}$$

$$S'^{(N)}(x) \approx 2\frac{C_{LUMO}(x)^2}{E_{LUMO} - \alpha}(-\beta) \tag{6}$$

Some workers used the similar equations to describe the reactivity of various molecules [53–57].

Stewart [29,58] implemented these parameters to describe the relatively reactive position in the frontier orbitals for the electrophilic, nucleophilic and radical reactions, respectively, as the electrophilic, nucleophilic and radical susceptibility, and their relative magnitudes of overlap or delocalization energy between the two frontier MO's of reagents, respectively, as the electrophilic, nucleophilic and radical superdelocalizability into MOPAC programs. The latter superdelocalizability, $S^{(E)}(x)$ and $S^{(N)}(x)$, on the other hand, are given as follows:

$$S^{(E)}(x) = \sum_{i=1}^{HOMO} \frac{2C_i(x)^2}{E^{E}_{LUMO} - E_i}(-\beta) \tag{7}$$

$$S^{(N)}(x) = \sum_{i=1}^{LUMO} \frac{2C_i(x)^2}{E_i - E^{N}_{HOMO}}(-\beta). \tag{8}$$

The choice of reagent energy, E^{E}_{LUMO} (LUMO energy of electrophile) and E^{N}_{HOMO} (HOMO energy of nuceophile), is crucial to the successful application of superdelocalizability especially to compare the reactivity against different reagents [25,58].

3.3.1. An analysis of electrophilic and nucleophilic reactivity for the A&HT's of model dyes in terms of the orbital energy differences

In order to analyse the electrophilic and nucleophilic reactivities for the A&HT's of the UD and D species of Orange I and II, the values of orbital energies and their electron densities at given positions in MOHO and LUMO for the above four species were estimated using the PM5 method (in the gaseous phase) and the PM5/COSMO method (in water) as shown in Tables 1 and 2. In reality, while the HT's of the UD species for Orange I and II may exist in water, in this paper, MO calculations were carried out for the hypothetical molecules shown in the tables, although some dyes may exist actually as the tautomers. The results are discussed to assess how the reactivity as well as the reaction sites varied with tautomers. (Considerable differences between the gaseous phase and water were recognized in the values of orbital energies for the D species of two dyes, but small ones for electron densities in the HOMO and LUMO. Some additional atomic positions where electron densities are relatively large besides the definite positions in the HOMO or LUMO are shown below the table. Unfortunately, findings of the results obtained using the COSMO method have not sufficiently been examined compared with the results evaluated in the gaseous phase, although the dyes and oxidants used can exist only in water.)

On applying the equations of superdelocalizability to the azo dye–oxidant system, correlation diagrams describing which combinations of HOMO and LUMO have smaller energy differences than others are illustrated in Figs. 1 and 2. The denominators of Eqs. (5) and (6), or of the energy differences between HOMO and LUMO are in the order of magnitude as follows:

$$\begin{array}{ll} & |\,E_{\mathrm{LUMO}} \text{ of UD(dye) species–} \\ & \qquad E_{\mathrm{HOMO}} \text{ of D(oxidant) species}\,| \\ << & |\,E_{\mathrm{HOMO}} \text{ of D(dye) species–} \\ & \qquad E_{\mathrm{LUMO}} \text{ of UD(oxidant) species}\,| \\ < & |\,E_{\mathrm{LUMO}} \text{ of D(dye) species–} \\ & \qquad E_{\mathrm{HOMO}} \text{ of UD(oxidant) species}\,| \\ < & |\,E_{\mathrm{HOMO}} \text{ of UD(dye) species–} \\ & \qquad E_{\mathrm{LUMO}} \text{ of D(oxidant) species}\,| \end{array} \tag{9}$$

The first and third terms describe the denominator of Eq. (6), the nucleophilic superdelocalizability, while the second and fourth terms that of Eq. (5), the electrophilic one. The interaction between the UD(dye) species and the D(oxidant) species describes the magnitude of k_2 of the second term in the right hand side of Eq. (2), although the first term of Eq. (9) has larger contribution than the fourth term of Eq. (9). Similarly, the interaction between the D(dye) species and the UD(oxidant) species describes the magnitude of k_3 of the third term in the right hand side of Eq. (2), although the second term of Eq. (9) has larger contribution than the third term of Eq. (9).

The other two schemes showing the interactions between species of UD(dye)–UD(oxidant) and D(dye)–D(oxidant) can be also drawn by

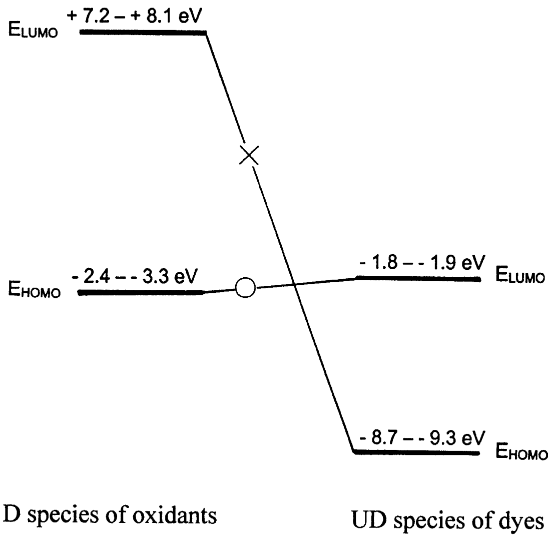


Fig. 1. Schematic diagram of the orbital interaction between UD species of dyes and D species of oxidants [(correlation: low (×) and high (○)].

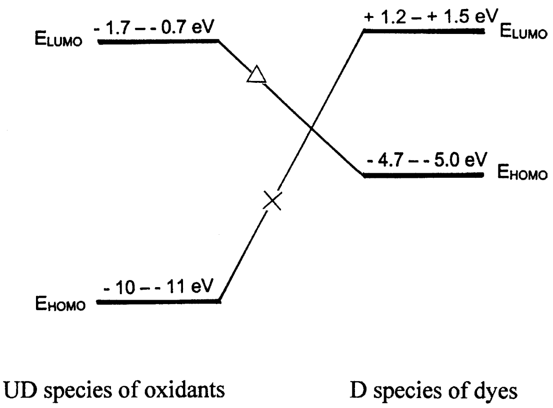


Fig. 2. Schematic diagram of the orbital interaction between D species of dyes and UD species of oxidants [correlation: low (×) and intermediate (△)].

exchanging the each partner of Eq. (9). Since the energy differences between HOMO and LUMO are larger than those shown in Figs. 1 and 2, the reactivity between them is smaller than that due to the mutual interaction between the UD and D species. The nucleophilic interaction between D(dye) species and D(oxidant) species may have some contribution, although it is suppressed considerably by the ionic repulsion between their D species [18,19,59–63]. These theoretical results may correspond to the experimental results that the values of k_1 and k_4 of Eq. (2) are negligible compared with those of k_2 and k_3, as mentioned above.

The above discussion shows that the differences between the E_{LUMO} of UD(dye) species and the E_{HOMO} of D(oxidant) species were the smallest of the differences between E_{HOMO} and E_{LUMO} for the oxidizing agent and azo dyes examined. Or oxidizing agents may act predominantly as nucleophiles.

3.3.2. Sites of electrophilic and nucleophilic reactions for A&HT's

As mentioned, chemical reactions occur at the position where mutual overlap of their frontier orbitals is most effective. Nucleophilic reactions may occur at the atomic position where the electron density of LUMO for UD(dye) species is largest, while the electrophilic reactions may occur at the position where the density of HOMO for D(dye) species is largest. The second and next largest positions may also contribute to these reactions, if the electron densities are comparable. The electron densities of HOMO and LUMO for the two tautomers of the UD and D species of the orange dyes are listed in Tables 1 and 2. (Concerning the numbering or symbolizing of atoms, see the footnote below Tables 1 and 2).

The nucleophilic reactions of HT's for the UD species of Orange I and II may occur predominantly at the N_{α} atom (the first nitrogen atom from the position of coupling, C1 carbon) and secondly at the C2 atom (the second atom of carbon in naphthalene). In the case of the hypothetical AT's, although in reality, little AT's of the dyes may exist in water, the reactions may occur predominantly at the N_{α} and secondly at the N_{β} atom. Although the positions of the double bonds shift with the AHT, the sum of the electron densities over the positions where the nucleophilic reaction may probably occur is comparable for two tautomers.

The electrophilic reactions of both the tautomers for the D(dye) species may occur predominantly at the N_{β} and secondly at the C1 atoms for Orange I and at the same positions but in reverse preference for Orange II. Reactions at the C13 atom (the α-carbon of the diazo component) may contribute also. On dissociation, little, if any, differences in the position of reactions were found for both tautomers of the dyes (cf. 3.1.2).

Thus, from the above discussions of dye–oxidant system via ionic reaction mechanism in terms of frontier orbital theory, the following conclusions are derived:

1. No large differences in reactivity are found between the tautomers for both the UD and D species of the dyes;
2. Which, electrophilic or nucleophilic, reaction of dye becomes dominant against oxidant is determined by the relative heights of the corresponding E_{HOMO} and E_{LUMO} of dye and oxidant;
3. The magnitude of the rate constants of reactions between a given dye and an electrophile or nucleophile of oxidant is determined by the relative sizes of differences between the E_{HOMO} and E_{LUMO}. The electrophilic reaction is determined by the difference between E_{HOMO} of dye and E_{LUMO} of oxidant, while the nucleophilic one by the difference between E_{LUMO} of dye and E_{HOMO} of oxidant. With a decrease in the difference, the corresponding reaction occurs more easily;
4. The positions of the reaction in dye molecules are determined by the electron densities of the frontier orbitals (HOMO for electrophilic reaction and LUMO for nucleophilic reaction);
5. The UD and D species of hypochlorous acid and hydrogen peroxide possess essentially similar oxidizing character;
6. The kinetic equation (Eq. (2)) is applied to a dye–oxidant system irrespective of the AHT of the dyes used.

Judging from the values of E_{HOMO} and E_{LUMO} by simple frontier orbital theory, the UD species of hypochlorous acid must not act as an extremely active electrophile, while the D species of hydrogen peroxide must act as a nucleophile and must not possess a higher reactivity than that of UD species. For electrophilic reactions, less energy differences between HOMO of D(dye) species and LUMO of UD(oxidant) species are favourable, while for nucleophilic reactions, less differences between LUMO of UD(dye) species and HOMO of D(oxidant) species are.

Thus, from the viewpoint of the ionic reaction between dyes and oxidant, there should be only a small difference in reactivity between hydrogen peroxide and hypochlorite. Differences in the reactivity between the two oxidants are not so large that the relative reaction rate for a substrate is $>10^5$. The results of Table 3 may imply that in the oxidation reaction of hypochlorous acid there may be some acceleration mechanisms such as a free radical mechanism. Recent reports on the reaction of hypochlorite showed a large contribution of free radical [64]. Coen et al. [49] reported recently the contribution to bimolecular reaction of dye radicals generated by the one-electron oxidation of the D species of azo dyes by hypochlorous acid, a substantial modification of previous papers on hypochlorite bleaching [9,12,50–52].

Some nucleophiles such as HO_2^-, ClO^-, RS^-, NH_2OH, N_2H_4, etc. are much more nucleophilic towards such electrophiles as carbonyl groups than one would expect from their pK_a values [26,27,59–61,65–69]. This means that the reactivity change is in the opposite direction to the pK_a change. (For example, although H_2O_2 is a stronger acid than H_2O by ca. 4 pK_a units, the ratios of reaction constants,$k_{HO_2^-}/k_{OH^-}$, were much larger than unity.) The increased reactivity of these nucleophiles has been called the α-effect. It was proved by the absence of an α-effect in the gas phase nucleophilic reactions of HO_2^- that the effect is attributed to a large decrease in the reactivity of the nucleophiles other than HO_2^- by hydration [68,69]. On the other hand, ClO^- may act as a nucleophile, since the electrophilic reactivity of this reagent may be lower than the nucleophilic one from the viewpoint of frontier orbital theory. Since it has not yet been reported that it has larger nucleophilic reactivity than that of HO_2^-, it may be required to reexamine their reaction behaviours before the reactivity of ClO^- is treated in terms of ionic reactions.

3.3.3. Reactivities of the tautomers for the UD and D species of Orange I and II against hydrogen peroxide

When the most general case of dye–oxidant interactions is considered for the UD and D species of the A&HT's of dyes and the UD and D species of oxidants, based on the procedure of the previous section, the possible number of combinations becomes 16 due to the HOMO–LUMO interaction between the species. Possible combinations of the interaction between the two tautomers of the UD and D species of a dye and the UD and D species of an oxidant are illustrated systematically in Table 4. To describe reaction kinetics between a dye and an oxidant, 16 second-order rate constants of the reaction are necessary, besides two values of K_T for the UD and D species of dye and two values of pK_a for the dye and oxidant. In principle, which constants of reaction rates are dominant or negligible may be estimated by simple frontier orbital theory.

The MO calculation for small molecules such as hydrogen peroxide is still open to debate even for molecules in the gaseous phase [70]. For example, ab initio calculation with an infinite basis set was applied for hydrogen peroxide to perform the geometry optimization in the gaseous phase [71]. (Even in case of neutral molecule in the gaseous phase, hydrogen peroxide needed a very large basis set in ab initio MO method. Too large a decrease in H_f in water, estimated by PM5/COSMO method, may imply a too small estimation of the molecular volume for the anions, since solvation of anions may increase with a decrease in the van der Waals radius, if comparison is made among constant number of charges.) To estimate the electrophilic and nucleophilic superdelocalizability of dyes, the values of E_{HOMO} and E_{LUMO} should be available. The energies of HOMO for the UD and D species of hydrogen peroxide were referred to [72]. The energies of

Table 4
Possible 16 combinations of interaction between a dye (UD&D species of A&H Ts) and an oxidant (UD&D species), and the positions with large reactivity [cf. Eqs. (5) and (6)]

No	Dye	Oxidant	Possible interaction		Kind and probable position of reaction for a dye		
			HOMO	LUMO	Reaction of dye	Tautomer	Probable position
1A	UD	UD	Dye	Oxidant	Electrophilic	AT	C1
						HT	Nβ, C1
1B			Oxidant	Dye	Nucleophilic	AT	Nα, Nβ
						HT	Nα, C2
2A	UD	D	Dye	Oxidant	Electrophilic	AT	C1
						HT	Nβ, C1
2B			Oxidant	Dye	Nucleophilic	AT	Nα, Nβ
						HT	Nα, C2
3A	D	UD	Dye	Oxidant	Electrophilic	AT	Nβ, C1
						HT	Nβ, C1
3B			Oxidant	Dye	Nucleophilic	AT	Nα, C13
						HT	Nα, C13
4A	D	D	Dye	Oxidant	Electrophilic	AT	Nβ, C1
						HT	Nβ, C1
4B			Oxidant	Dye	Nucleophilic	AT	Nα, C13
						HT	Nα, C13

LUMO were obtained by MO calculations. The results are listed in Table 5.

From the present state of MO theory for small molecules, the PM5 method was applied to estimate the reactivity of azo dyes towards oxidizing agents. All 16 approximate values of nucleophilic and electrophilic superdelocalizabilities, $S'^{(E)}(x)$ and $S'^{(N)}(x)$, for Orange I and II in the reaction with hydrogen peroxide were calculated using Eqs. (5) and (6) from the E_{HOMO}, E_{LUMO} and electron densities in the frontier orbitals, HOMO and LUMO of dyes (data listed in Table 1). (In this calculation, the value of β was fixed 1 eV to make $S(x)$ dimensionless.) Which values, the energy differences between the frontier orbitals of dye and reagent, and the electron densities in the frontier orbitals of dye, determine the reactivity is examined. The results are listed in Table 6.

In the estimation of superdelocalizabilities, only the atomic positions whose electron densities in the corresponding orbitals were larger than 0.1 were taken into consideration. The values of

Table 5
Enthalpy of formation, H_f (kcal mol^{-1}), and energies of HOMO and LUMO (eV) for oxidants, estimated with various MO methods

Method or source		H_2O_2	HO_2^-	HClO	ClO^-	$^1O_2$
PM3[a]	H_f	−40.549	−23.633	−33.849	−32.888	79.883
	E_{HOMO}	−11.570	2.499	−10.483	−2.581	−12.358
	E_{LUMO}	1.712	11.518	0.311	9.577	−3.156
PM5	H_f	−37.063	−51.092	−20.195	−41.221	88.698
	E_{HOMO}	−11.053	−2.992	−10.912	−3.281	−11.794
	E_{LUMO}	−0.700	7.467	−1.694	6.617	−4.729
PM5/COSMO	H_f	−53.051	−176.734	−30.969	−149.265	87.080
	E_{HOMO}	−11.158	−11.236	−10.990	−10.666	−11.878
	E_{LUMO}	−0.531	−0.172	−1.408	−0.534	−4.680
H_f obs. in water [73]	H_f	−44.9[b]	−38.32(aq)	−28.68(aq)	−25.6(aq)	

[a] PM3 method included in MOPAC 2002 [29].

[b] Liquid.

Table 6
Electrophilic and nucleophilic superdelocalizabity, $S'^{(E)}(x)$ and $S'^{(N)}(x)$, at the positions with largest and next largest reactivity for the reaction of Orange I and II with hydrogen peroxide [cf. Table 4 and Eqs. (5) and (6)][a]

Dye	Species	Tautomer	Reaction	Superdelocalizability (position)	
				H_2O_2[b]	HO_2^-[c]
Orange I	UD	AT	Electrophilic	$S'^{(E)}=0.0528(C1)$	$S'^{(E)}=0.2484(C1)$
		HT		$S'^{(E)}=0.0662(N_\beta)$	$S'^{(E)}=0.4640(N_\beta)$
		AT	Nucleophilic	$S'^{(N)}=0.0420(N_\alpha)$	$S'^{(N)}=0.6092(N_\alpha)+0.5354(N_\beta)=1.1446$
		HT		$S'^{(N)}=0.0368(N_\alpha)$	$S'^{(N)}=0.6188(N_\alpha)+0.5000(C2)=1.1188$
	D	A&H	Electrophilic	$S'^{(E)}=0.1112(N_\beta)+0.1106(C1)=0.2218$	$S'^{(E)}=0.0856(N_\beta)+0.0820(C1)=0.1676$
		A&H	Nucleophilic	$S'^{(N)}=0.0308(N_\alpha)$	$S'^{(N)}=0.1056(N_\alpha)$
Orange II	UD	AT	Electrophilic	$S'^{(E)}=0.0542(C1)$	$S'^{(E)}=0.2862(C1)$
		HT		$S'^{(E)}=0.0584(N_\beta)$	$S'^{(E)}=0.3270(N_\beta)$
		AT	Nucleophilic	$S'^{(N)}=0.0462(N_\alpha)$	$S'^{(N)}=0.8208(N_\alpha)+0.6524(N_\beta)=1.4732$
		HT		$S'^{(N)}=0.0490(N_\alpha)$	$S'^{(N)}=0.9928(N_\alpha)+0.6126(C2)=1.6054$
	D	A&H	Electrophilic	$S'^{(E)}=0.1108(N_\beta)+0.1388(C1)=0.2496$	$S'^{(E)}=0.0772(N_\beta)+0.0966(C1)=0.1738$
		A&H	Nucleophilic	$S'^{(N)}=0.0142(N_\alpha)$	$S'^{(N)}=0.0474(N_\alpha)$
N-Methyl-Orange I			Electrophilic	$S'^{(E)}=0.0580(N_\beta)$	$S'^{(E)}=0.3862(N_\beta)$
			Nucleophilic	$S'^{(N)}=0.0460(N_\alpha)$	$S'^{(N)}=0.5416(N_\alpha)+0.3406(C2)=0.8822$
O-Methyl-Orange I			Electrophilic	$S'^{(E)}=0.0178(C1)$	$S'^{(E)}=0.0790(C1)$
			Nucleophilic	$S'^{(N)}=0.0420(N_\alpha)$	$S'^{(N)}=0.5524(N_\alpha)+0.4752(C2)=1.0276$

[a] MO calculation was carried out for molecules in the gas phase.
[b] H_2O_2: $E_{HOMO}=-11.2$ eV; $E_{LUMO}=-0.7$ eV (PM5).
[c] HO_2^-: $E_{HOMO}=-2.4$ eV [72]; $E_{LUMO}=8.1$ eV (from difference by PM5).

$S'^{(E)}(x)$ and $S'^{(N)}(x)$ may describe semiquantitatively the relative contribution of the respective HOMO–LUMO interaction to the reactivity, although the proportionality factors of $S'^{(E)}(x)$ and $S'^{(N)}(x)$ to the rates of reaction may change with sites because of the different mechanism of reactions. Their values may be so roughly proportional to the rates that no strict comparison between experimental results may be valid. Irrespective of such the restrictions and limitations, the six values of $S'^{(E)}(x)$ and $S'^{(N)}(x)$ of Orange I and II against hydrogen peroxide and the perhydroxyl ion may imply the validity of their experimental results reported so far (cf. Table 3) and exhibit clearly their whole reaction behaviours. Thus, the predominant reaction between both the dyes and hydrogen peroxide was proved to be a nucleophilic reaction between the UD(dye) species and the D(oxidant) species, which correlates with the values of k_2 of Eq. (2). In the reactions of AT's, predominantly α- and secondly β-nitrogen participates, while in that of HT's, predominantly α-nitrogen and secondly the C2-carbon participates. Two tautomers are shown to possess nearly similar reactivity against oxidants each other. $S'^{(N)}(x)$ of Orange I is smaller than that of Orange II in reverse to the experimental results of Table 3. The present frontier orbital theory may not be accurate enough to describe such a minute comparison.

The secondly dominant term of the superdelocalizabilities is the electrophilic interactions between the D(dye) species and the UD(oxidant) species, which correlate with the values of k_3 of Eq. (2). Although $S'^{(E)}(x)$ of two dyes against hydrogen peroxide is a fourth or a fifth of $S'^{(N)}(x)$ corresponding to the predominant terms, the values of k_3 were experimentally estimated to be negligible, compared with the values of k_2 [74]. Moreover, $S'^{(E)}(x)$ of the UD species for two dyes against perhydroxyl ion, the thirdly dominant term of interactions, is a half or a third of $S'^{(N)}(x)$ corresponding to the predominant terms. Since no one can experimentally determine the contribution of this interaction to the values of k_2, the values of k_2 may contain this term. Although there are the other interactions of minor contributions, which correlate with the values of k_1 and k_4 in Eq. (2), they may be negligible as shown experimentally and by this MO theory.

As mentioned above, changes in the reactivity of dyes and oxidants with dissociation are caused by a large rise in the E_{HOMO} and E_{LUMO}. The increases in E_{HOMO} and E_{LUMO} for dyes in the gaseous phase are about 4 and 3 eV, respectively, while those for hydrogen peroxide are about 9 and 10 eV for both orbitals. The differences in the rise of E_{HOMO} and E_{LUMO} result in the reversion of the predominance between electrophilic and nucleophilic reactions. Thus, even if these results of MO calculations contained considerable errors, the predominance between both the kinds of reaction cannot be reversed. Moreover, the correlations between the observed results in Table 3 and the calculated results listed in Table 6 are good enough to conclude that the PM5 calculation for molecules in the gaseous phase illustrates well the real reaction behaviours in dye–oxidant system.

Gregory and Stead [8] used the *O*- and *N*-methyl derivatives in the oxidation reaction of azo dyes with hypochlorite as model compounds of the A&HT's. Oakes et al. [9,12,51] and Tamura et al. [47,48] determined their second-order rate constants of reaction with hydrogen peroxide and hypochlorous acid (cf. Table 3) and showed the reaction mechanism for the HT's of azo dyes. The above discussions explain the essential reason why such interactions between HOMO and LUMO of a given dye and an oxidant are dominant. The larger change in reactivity given by dissociation of dyes and oxidants can be attributed to a large rise in both the E_{HOMO} and E_{LUMO} accompanied with a relatively small change in their energy differences. As the result, perhydroxyl ions may act as a nucleophile against Orange I and II, while hydrogen peroxide may have small or little reactivity as an electrophile. Although there remains some uncertainty in the present simple theory, the values of k_2 may contain an electrophilic contribution. This may be examined by the separation and analysis of the reaction products. According to Oakes and Gratton [11,12], no reaction products could be separated due to the further rapid decomposition into small fragments. This fact may prove the multiple sites of reaction for the original dyes and/or further reaction of reaction products with oxidants.

3.4. *Reactivity of* N- *and* O-*methyl Orange I against hydrogen peroxide*

The introduction of methyl groups into the N_β atom or phenolic oxygen atom results in a small rise in both the E_{HOMO} and E_{LUMO} accompanied with small shifts in their differences, as shown in Table 1. The introduction seems to cause little change in electronic structure. They may be utilized as the respective model compounds of the A&HT's, although the *O*-methyl compounds may have more identical structure with the original AT's than the *N*-methyl ones. Using the same method as in Section 3.3 (cf. Table 1), the values of $S'^{(\mathrm{E})}(\mathrm{x})$ and $S'^{(\mathrm{N})}(\mathrm{x})$ of the *N*- and *O*-methyl derivatives of Orange I against hydrogen peroxide and perhydroxyl ion were calculated as shown in Table 6. It can be concluded that these derivatives were oxidized with a nucleophile, namely the perhydroxyl ion, while reactions with hydrogen peroxide were negligible. Due to the shift of orbital energy levels, they must not possess the same reactivity as the original A&HT's, respectively, as being implied also by other experiments [9], although their reaction sites are the same as those of corresponding tautomers due to the similarity of electronic structures.

3.5. *Reactivity of phenylazonaphthol dyes against singlet oxygen*

In an investigation on the photo-oxidation reaction of the HT's for a series of phenylazonaphthols with singlet molecular oxygen, Griffiths and Hawkins [75] reported a mechanism showing a decomposition of the original dye and a generation of 1,4-naphthoquinone and a bisazo compound. In this mechanism, the photo-oxidation of hydroxyazo dyes proceeds via the oxidation of HT's (ene reaction) with singlet oxygen. While these results seem to prove the non-reactivity of AT's in the photo-oxidation, the present analysis suggests they may also lead to reverse conclusions. It may be that the reactivity of phenylazonaphthols against singlet oxygen are only slightly influenced by the AHT but markedly influenced by the electron-withdrawing substituents in the phenyl ring. For a clearer understanding of these circumstances, the Sections 3.5.1 (AHT and 3.5.2 (reactivity against singlet oxygen) present analyses of Griffiths and Hawkins's results [76] using the present MO method.

3.5.1. AHT of 4-phenylazo-1-naphthols and 1-phenylazo-2-naphthols

An analysis of AHT by the previously described PM5 method [28] may help elucidate the essential properties of azo dyes, even though this method is applicable only to azo dyes in the gaseous phase or water. Tables 7 and 8 show estimations of the values of H_f for 4-phenylazo-1- and 1-phenylazo-2-naphthols in both the media, respectively. Table 8 lists both *m*-methyl and *m*-methoxy derivatives (cf. footnote below Table 9). Table 9 lists the differences in H_f between the tautomers, in order to enable discussion on which A&HT's have higher stability in the two media.

The differences in H_f between the two tautomers may indicate that all but a few of the hypothetical molecules of 1-phenylazo-2-naphthols exist as AT's in the gaseous phase and as HT's in water. The overwhelmingly majority of the derivatives of 4-phenylazo-1- and 1-phenylazo-2-naphthols exist as HT's in water, although several exist predominantly as HT's in the gaseous phase. *p*-Methoxy derivatives of phenylazo-1- and-2-naphthols exist predominantly as AT's in the gaseous phase. Shifts to AT's via the introduction of *p*-methoxy groups were confirmed in spectroscopic studies conducted in various solvents by Burawoy et al. [3], Reeves and Kaiser [43], and Oakes et al. [10]. In experiments by Griffiths and Hawkins [76], to assign the 4-phenylazo-1-naphthols to the AT's and/or HT's, the assignment of tautomers was almost reverse to that demonstrated in the gaseous phase by the present MO method, as illustrated in Table 9. If their assignment to A&HT's [76] is assumed to be reverse, then the values of $1/K_E$ (cf. footnote below Table 9 for the definition of K_E), approximate the population ratio of HT/AT for the molecules in the gaseous phase by the MO method. Moreover, their results can also be used to demonstrate that the AT's such as the *p*-methoxy derivatives quickly faded due to photo-oxidation, supporting a conclusion opposite to that which they proposed.

In the case of 1-phenylazo-2-naphthols, all the derivatives exist predominantly as HT's in both the gaseous phase and water, with the exception of the *p*-methoxy derivative in the gaseous phase. In all but a few cases, no regular correlation seems to

Table 7
Enthalpy of formation, H_f (kcal mol^{-1}), HOMO and LUMO energies, E_{HOMO} and E_{LUMO} (eV), electron density of HOMO and LUMO, d_{HOMO} and d_{LUMO}, at given atoms for 4-(substituted phenylazo)-1-naphthols in the gas phase, and H_f (kcal mol^{-1}) in water, estimated by semiempirical molecular orbital (PM5 and COSMO) method

Substituent		*p*-OMe		*p*-Me		H		*p*-Cl		*m*-Cl		*p*-COCH$_3$	
Tautomer		AT	HT	AT	HT	AT	HT	AT	HT	AT	HT	AT	HT
M.W.		278.310		262.310		248.284		282.729		282.729		290.321	
H_f		31.347	31.842	59.997	60.054	68.625	68.198	60.577	60.512	60.906	60.478	26.691	25.838
E_{HOMO}		−8.224	−8.557	−8.249	−8.601	−8.268	−8.709	−8.395	−8.793	−8.416	−8.871	−8.460	−8.906
E_{LUMO}		−1.127	−1.389	−1.098	−1.369	−1.147	−1.394	−1.290	−1.494	−1.307	−1.495	−1.423	−1.572
d_{HOMO}	C1	0.118	0.001	0.126	0.001	0.131	0.001	0.127	0.001	0.131	0.001	0.129	0.001
	C4	0.172	0.082	0.185	0.104	0.195	0.116	0.192	0.100	0.199	0.109	0.198	0.108
	N_α	0.021	0.051	0.016	0.060	0.011	0.071	0.011	0.065	0.008	0.076	0.014	0.074
	N_β	0.052	0.215	0.057	0.254	0.059	0.277	0.060	0.255	0.061	0.271	0.066	0.276
d_{LUMO}	C1	0.129	0.146	0.133	0.146	0.134	0.145	0.123	0.144	0.126	0.144	0.109	0.140
	C2	0.012	0.117	0.012	0.116	0.012	0.117	0.009	0.120	0.010	0.119	0.007	0.120
	C3	0.102	0.194	0.103	0.193	0.105	0.192	0.103	0.190	0.104	0.189	0.190	0.185
	N_α	0.182	0.173	0.182	0.174	0.186	0.174	0.194	0.172	0.196	0.172	0.180	0.172
	N_β	0.203	0.025	0.203	0.026	0.204	0.025	0.199	0.023	0.200	0.022	0.094	0.021
H_f in water		9.402	3.899	42.417	36.179	50.810	44.344	43.291	37.120	42.677	37.151	0.656	−7.731

Table 8

Enthalpy of formation, H_f (kcal mol^{-1}), HOMO and LUMO energies, E_{HOMO} and E_{LUMO} (eV), electron density of HOMO and LUMO, d_{HOMO} and d_{LUMO}, at given atoms for 1-(substituted phenylazo)-2-naphthols in the gas phase and H_f (kcal mol^{-1}) in water, estimated by semiempirical molecular orbital (PM5 and COSMO) method

Substituent		*p*-OMe		*p*-Me		*m*-Me		*m*-OMe		H		*p*-Cl		*m*-NO$_2$	
Tautomer		AT	HT	AT	HT	AT	HT	AT	HT	AT	HT	AT[a]	HT	AT[*1]	HT
M.W.		278.310		262.310		262.310		278.310		248.284		282.729		293.281	
H_f		29.896	30.176	58.437	58.205	58.792	58.268	30.830	30.201	66.794	66.445	59.057	58.888	63.676	63.606
E_{HOMO}		−8.325	−8.385	−8.361	−8.411	−8.414	−8.469	−8.484	−8.507	−8.437	−8.484	−8.523	−8.594	−8.807	−9.053
E_{LUMO}		−1.260	−1.379	−1.233	−1.350	−1.246	−1.360	−1.349	−1.446	−1.271	−1.386	−1.435	−1.514	−1.783	−1.737
d_{HOMO}	C1	0.087	0.002	0.093	0.002	0.096	0.002	0.092	0.002	0.097	0.002	0.094	0.001	0.095	0.000
	C4	0.188	0.143	0.206	0.164	0.217	0.171	0.208	0.152	0.219	0.169	0.213	0.150	0.231	0.146
	N_α	0.019	0.025	0.014	0.026	0.010	0.029	0.009	0.026	0.009	0.031	0.009	0.030	0.003	0.051
	N_β	0.065	0.226	0.072	0.248	0.076	0.259	0.074	0.238	0.077	0.262	0.076	0.251	0.085	0.265
d_{LUMO}	C1	0.132	0.180	0.134	0.179	0.138	0.180	0.136	0.179	0.136	0.181	0.129	0.180	0.098	0.174
	C2	0.022	0.070	0.023	0.070	0.023	0.070	0.022	0.068	0.023	0.071	0.019	0.069	0.012	0.063
	C3	0.108	0.145	0.110	0.144	0.111	0.144	0.113	0.146	0.111	0.145	0.110	0.147	0.090	0.148
	N_α	0.190	0.178	0.191	0.179	0.193	0.179	0.199	0.178	0.194	0.174	0.210	0.173	0.179	0.172
	N_β	0.195	0.056	0.195	0.057	0.196	0.057	0.194	0.053	0.195	0.054	0.190	0.049	0.147	0.036
H_f in water		9.713	5.737	43.250	37.634	43.074	37.898	10.859	6.143	51.050	46.015	43.503	38.719	38.470	32.836

[a] d_{HOMO}, C10: 0.111.

Table 9

Analysis of photosensitized fading of 4-phenylazo-1-naphthols and 1-phenylazo-2-naphthols [76] in benzene–methanol (4:1) solution and the estimation of AHT and superdelocalizability, $S'^{(E)}$ against singlet molecular oxygen by semiempirical MO (MOPAC 2002, PM5 and COSMO) method[a]

Substituent	*k* [76][b]	k_{obs}	Hammett σ-values	Ratio of K_E[c] [76]	$H_f^{AT}-H_f^{HT}$[d]		$S'^{(E)}$ for AT[e]				$S'^{(E)}$ for HT		
					Gas phase	Water	C4	C1	N_β	Sum	N_β	C4	Sum
4-(substituted phenylazo)-1-naphthols													
p-OMe	3.9	0.95	−0.28	3.1	−0.495	5.503	0.201	0.138	–	0.339	0.210	0.080	0.290
p-Me	1.9	0.26	−0.14	6.3	−0.057	6.238	0.213	0.145	–	0.358	0.243	0.099	0.342
H	1.0	0.37	0	1.7	0.427	6.466	0.222	0.149	–	0.371	0.252	0.106	0.358
p-Cl	1.0	0.40	0.22	1.5	0.065	6.171	0.204	0.135	–	0.339	0.211	0.083	0.294
m-Cl	0.56	0.24	0.37	1.3	0.428	5.526	0.209	0.137	–	0.346	0.230	0.092	0.322
tp-Ac	0.13	0.13	0.47	ca. 0	0.853	8.387	0.203	0.132	–	0.335	0.230	0.090	0.320
1-(substituted phenylazo)-2-naphthols													
p-OMe	4.0	1.91	−0.28	1.1	−0.280	3.976	0.207	0.096	0.072	0.375	0.241	0.153	0.394
p-Me	1.4	0.40	−0.14	2.5	0.232	5.616	0.223	0.101	0.078	0.402	0.261	0.173	0.434
H	1.0	0.52	0	0.93	0.349	5.035	0.227	0.101	0.079	0.408	0.265	0.171	0.436
m-Me[f]	0.82?	0.44?	−0.06	0.85?	0.524	5.176	0.228	0.101	0.080	0.409	0.264	0.175	0.439
mt-OMe[f]	0.82?	0.44?	0.10	0.85?	0.628	4.716	0.211	0.093	0.075	0.379	0.238	0.152	0.390
p-Cl	0.45	0.23	0.22	0.98	0.169	4.784	0.212	0.093	0.076	0.381	0.241	0.144	0.385
m-NO$_2$	0.16	0.084	0.71	0.90	0.070	5.634	0.201	0.083	0.074	0.358	0.208	0.115	0.323

[a] E_{LUMO} for singlet oxygen = −6.51 eV.

[b] *k* = relative rate of fading of HTs, estimated by Griffiths and Hawkins [76].

[c] K_E = HT/AT (the population ratio of HTs and ATs, estimated by Griffiths and Hawkins [76]).

[d] Minus of difference means that ATs have higher stability than HTs.

[e] $S'^{(E)}(C4 + C1 + N_\beta)$ for ATs of 1-(substituted phenylazo)-2-naphthols, while $S'^{(E)}(C4 + C1)$ for ATs of 4-(substituted phenylazo)-1-naphthols, since the electron densities at N_β are smaller than 0.06.

[f] 4d = *m*-OMe or *m*-Me?[76] (because of the misprint, it is impossible to decide the substituent. From the differences in H_f, *m*-methyl group may be regarded as the substituent. But, *m*-OMe is also listed for the comparison.)

be found between K_E [76] and K_T values in the gaseous phase. However, given that the K_E values lie within narrow range around 1, the scattering of the K_E and K_T values [cf. Eq. (1)] may stay within the margin of experimental error. The K_E value for the *p*-methoxy derivative is also contrary to the corresponding value estimated by the MO method in the gaseous phase.

Table 9 lists the derivatives of phenylazonaphthols in the order of the *k* values (the relative rate of fading of HT's, cf. 3.5.2). Several earlier papers have demonstrated that the K_E values are not always proportional to the Hammett σ-values or dependent upon the substituent effects [32,37,43]. [Strictly speaking, Hammett (original) constants cannot be applied to this case, since the photo-oxidative reaction occurs either at the position of N_β of the azo group outside the phenyl ring or at the position of the azo coupling in the naphthalene ring beyond the azo group (cf. Table 4). The σ-values that usually express the substituent effects in the same phenyl ring are used as an approximate standard.] The population ratios are dependent upon the solvation but not proportional to the dielectric constant of medium or the substituent effects of azo dyes. When the AHT of hydroxyazo dyes were experimentally examined, all the dyes were assigned to the HT's. However there must be a few to the AT's, shown by the estimation using PM5 method [28]. The only exceptions were a few *o*′-sulfo derivatives [1].

Future studies should re-examine the fundamentals of the assignment of the 4-phenylazo-1- and 1-phenylazo-2-naphthols, as well as the other azo dyes, to the A&HT's.

3.5.2. MO analysis of the reactivity against singlet oxygen

Notwithstanding the disagreement in the population ratio between the original report and the analyses by absorption spectra [3,43] and MO calculations, this paper continues to re-examine the rate of photosensitized fading estimated in the solvent mixture [76]. Griffiths and Hawkins [76] concluded that the photo-oxidative fading occurred only via the ene reaction of the HT's with $^1O_2$. They calculated the rate of fading (*k*) of the HT's relative to the total rate of fading by multiplying a factor of $(1 + K_E)$. This transformation is valid only if the rate of fading of the AT's is zero. If the rate of fading of the AT's is not zero, this treatment attributes all of the dye fading to the fading of the HT's. Griffiths and Hawkins's data are listed in Table 9.

3.5.2.1. Applicability of the Hammett equation. When the *k* values were plotted against the Hammett σ-values, the curves drawn up to show their correlations indicated that none of the *k* values obeyed the Hammett equation, as illustrated in Fig. 3. It follows that the *k* values provided no proofs of the exclusive fading of the HT's. Alternatively, if the K_E values are reversed, this paper may indicate that the fading of the AT's was also dependent on the properties of dyes themselves. (Coefficients are omitted from Figs. 3 and 4, since

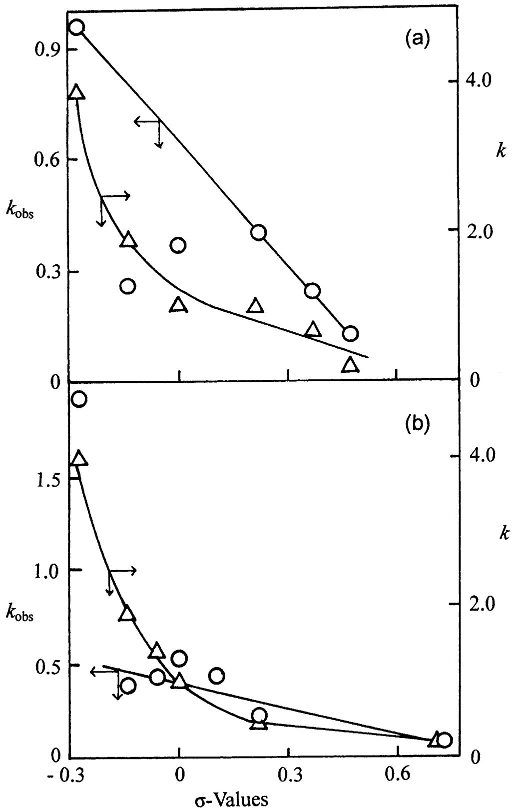


Fig. 3. Hammett plots of the relative rates of fading, *k* (△) [76] and k_{obs}(○), against σ-values for: (a) 4-phenylazo-1-naphthols; and (b) 1-phenylazo-2-naphthols (see text).

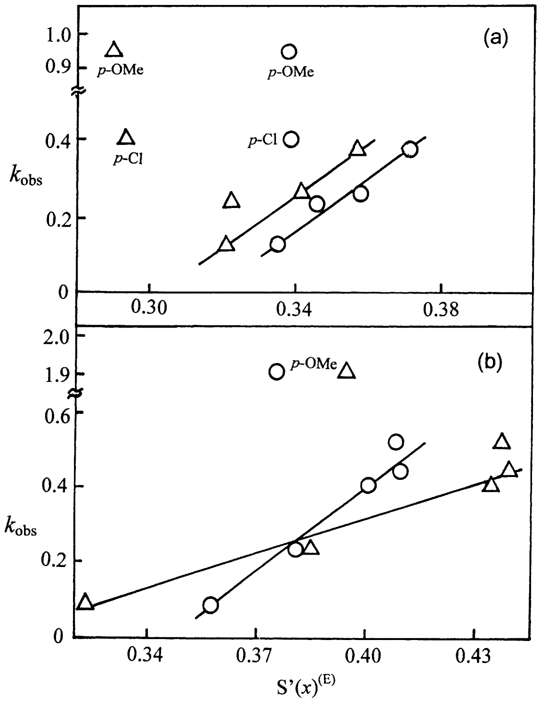


Fig. 4. Relationship between electrophilic superdelocalizability, $S'(x)^{(E)}$, and the relative rates of fading, k_{obs}, for the AT's (○) and HT's (△) of: (a) 4-phenylazo-1-naphthols; and (b) 1-phenylazo-2-naphthols (see text).

it would be meaningless to give them. The correlation coefficients that express the correlation between the k values and σ-values may depend on the number of samples, if the number is small. The number of plots is too small to reasonably express this correlation.)

The present authors also tried to use the data to draw another conclusion, namely, to determine when the k values were transformed. This attempt was made by dividing a factor of $(1+K_E)$ into the apparent relative rate of fading, k_{obs}, for the total concentration of dyes. Plotting the k_{obs} values against the Hammett σ-values usually gave a linear correlation, as illustrated in Fig. 3(a) and (b) for two series of phenylazonaphthols. As explained above, the Hammett (original) constants cannot be applied to the reactions of phenylazonaphthols with singlet oxygen beyond the azo groups, or to the reactions of the azo groups themselves (cf. 3.5.1). However, five (see footenote below Table 9.) derivatives of the 2-naphthols and four derivatives of the 1-naphthols may fit the Hammett plots. Two derivatives with no substituent and p-methyl of 1-naphthol series do not obey the rule and two derivatives with no substituent and p-methoxy of 2-naphthol series do not obey the rule (see text). This condition may indicate that *in most cases*, the total rate of fading of phenylazonaphthols obeys the Hammett equation beyond azo groups. Thus, as mentioned above and reported previously [77], the A&HT's possess the same oxidative fading as each other. Since the two tautomers have nearly the same E_{HOMO} and E_{LUMO} with shifts of double bonds, both should exhibit the same reactivity to singlet oxygen but react via separate mechanisms.

3.5.3. Analysis by frontier orbital theory

This section will examine whether MO theory is suitable for interpreting the fading behaviours of phenylazonaphthols, including the exceptional dyes that do not obey the Hammett equation. This is accomplished by analysing the reaction of hydroxyazo dyes with singlet molecular oxygen using the simple frontier orbital theory. In spite of its electronic structure as a biradical, singlet oxygen is recognized to behave as an electrophile that reacts with electron-rich aromatic compounds [77–79]. Since azo dyes exist as the AT's or HT's of the UD species, the frontier orbital interaction occurs only between the LUMO of singlet oxygen and the HOMO of dyes. The values of $S'^{(E)}(x)$ were calculated for the A&HT's of 4-(substituted phenylazo)-1-naphthols and 1-(substituted phenylazo)-2-naphthols (listed in Table 9). Figs. 4(a) and (b) plot the relationships between the k_{obs} and $S'^{(E)}(x)$ values of the A&HT's for two series of phenylazonaphthols. As a whole, they exhibit good correlation irrespective of AHT and the growing scale of $S'^{(E)}(x)$. The p-methoxy derivatives of the two series deviate completely, and the p-chloro derivatives of the 1-naphthols deviate considerably. The MO treatment also proved applicable to the dyes that disobeyed the Hammett equation, although it was only weakly applicable to the strong electron-donating groups.

The AHT problem still remains to be discussed. Unfortunately, no precise determination of K_E is possible, given that the MO calculation is unsuitable for solvent mixtures, and that unanswered questions remain on the original determination, as mentioned above. In spite of these restrictions, the relatively small differences in $S'^{(E)}(x)$ between the two tautomers of the 1-naphthol series suggest that Fig. 4(a) may explain the good correlation between $S'^{(E)}(x)$ and values of k_{obs}.

In the case of the 2-naphthol series, the only exception is *p*-methoxy derivative, assuming that the *m*-methyl derivative is used as shown in the figure. The plots of the $S'^{(E)}(x)$ values of the two tautomers against the k_{obs} values crossed each other, indicating a reversal of the magnitude of $S'^{(E)}(x)$ between the two tautomers. The differences in $S'^{(E)}(x)$ between the two tautomers in the 2-naphthol series were larger than those in the 1-naphthol series except for the derivatives with intermediate property. The values rose when the electron-withdrawing or electron-donating property of the substituents increased. In spite of these limitations, Fig. 4(b) may also explain the fair correlation between $S'^{(E)}(x)$ and the k_{obs} values for the 2-naphthol series.

In general, the simple frontier orbital theory can describe the reactivity of azo dyes against singlet oxygen with some restrictions. The differences in the reactivities between two tautomers are relatively small. Although the PM5 method may work well in treating the reaction behaviours of phenylazonaphthols with electron-withdrawing groups against singlet oxygen, it appears to work poorly in treating those with electron-donating groups. Although there were relatively small differences between the $S'^{(E)}(x)$ values of the two tautomers, the reaction sites of the tautomers were markedly different, as shown in Tables 7–9. This was because the reactions of the two tautomers obey different mechanisms against singlet oxygen [77]. Griffiths and Hawkins [76] reported the *k* values as the relative rates against the reference compounds, whereas the present analyses indicate that when a comparison is made between derivatives with the same substituent, the real rates of fading for 2-naphthols are larger than those for 1-naphthols.

From the present analyses of photosensitized fading for two series of phenylazonaphthols and their substituent effects reported by Griffiths and Hawkins [76], the following conclusions can be obtained:

1. The values of k_{obs} depend on the values of $S'^{(E)}(x)$.
2. There are only small differences between the $S'^{(E)}(x)$ values of the two tautomers. The two tautomers possess nearly the same reactivity against singlet oxygen.
3. The differences between the reaction of the two tautomers are due to different reaction mechanism given by their reaction sites.
4. The reactions of azo dyes with singlet oxygen occur at atomic sites with high electron densities in HOMO. More than one reaction sites emerge when there are atomic positions with relatively high electron density.
5. The substituents in a series of dyes have large effects on the electron densities at the given atomic positions but small effects on the HOMO energy.
6. The HOMO energies depend upon the basic structure of dyes.
7. These rules also hold in the reactions of dyes with oxidizing agents.

4. Summary

The AHT, the acid–base equilibrium and the reactivity of Orange I and II as well as 4-phenylazo-1-naphthols and 1-phenylazo-2-naphthols against oxidants were analysed by estimating the H_f values in both the gaseous phase and water using semi-empirical MO methods (PM5 and COSMO). The following conclusions were obtained:

1. The HT's of the UD species of the two orange dyes have higher stability in water than the AT's. While the D species of the A&HT's for the two orange dyes have almost the same stability each other.
2. Both the UD&D species cause the AHT and the acid–base equilibrium. An assumption that the HT's have smaller pK_a values than the AT's can explain reasonably some exceptional experimental results. It is a possible explanation of unsolved problems.

3. According to the frontier orbital theory, the A&HT's of the UD species have nearly similar reactivity as each other against oxidants including singlet molecular oxygen, although the positions of highest reactivity are different.
4. The dissociation of hydroxyazo dyes and/or oxidants changes their mutual reactivity due to a rise in E_{HOMO} and E_{LUMO}. Both the tautomers of the D species of orange dyes have almost the same electronic structure as each other irrespective of different sites of ionization. The A&HT's of the D species possess the same reactivity as each other and cause reactions at the same position.
5. The *N*- and *O*-methyl derivatives of Orange I have similar electronic structures to those of the original H&AT's, respectively. However, since the *N*- and *O*-methyl derivatives have higher orbital energy than the original tautomers, they have lower reactivity than the corresponding original ones.
6. The AHT and the reactivity of 4-phenylazo-1-naphthols and 1-phenylazo-2-naphthols can be treated by the same methods as above to gain the same conclusion. Their A&HT's should have similar reactivity to each other.
7. Actually, since either tautomer exists predominantly in many cases, the reactivity of hydroxyazo dyes is that of either tautomer for the dyes. But the differences in the reactivity between tautomers are small. The reactivity of the dyes is dependent upon the essential property of the dye itself but not upon the AHT.

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References

[1] Zincke T, Bindewald H. Über Phenylhydrazin-derivate des α- und β-Naphtholchinons. Identität des α-Derivats mit dem Azoderivat des α-Naphthols. Berichte der Deutschen Chemischen Gesellschaft 1884;17:3026–33.

[2] Kuhn R, Bär F. Über die Konsitution der Oxy-azo-verbindungen. Justus Liebigs Annalen der Chemie 1935;516: 143–55.

[3] Burawoy A, Salem AG, Thompson AR. The nature of the internal hydrogen bond. I. Tautomerism of 1-arylazo-2-naphthols. Journal of the Chemical Society 1952:4793–8.

[4] Burawoy A, Salem AG, Thompson AR. The effect of the solvents on the tatomeric equilibria of 4-arylazo-1-naphthols and the ortho-effect. Journal of the Chemical Society 1953:1443–7.

[5] Müller JB, Blangey L, Fierz-David HE. Spektroscopische Untersuchung an Orange I und Orange II. Helvetica Chimica Acta 1952;35:2579–89.

[6] Fischer E, Frei YF. Tautomerism and geometrical isomerism of arylazo-phenols and-naphthols. Part 1. 4-Phenylazo-1-naphthol. Journal of the Chemical Society 1959: 3159–63.

[7] Zollinger H. Chemie der azofarbstoffe. Basel: Birkhäuser; 1958; Azo and Diazo Chemistry, aliphatic and aromatic compounds (Nursen HE, trans.). Interscience; 1961.

[8] Gregory P, Stead CV. The degradation of water-soluble azo compounds by dilute sodium hypochlorite solution. Journal of the Society of Dyers and Colourists 1978;94: 402–7.

[9] Oakes J, Gratton P. Kinetic investigation of azo oxidation in aqueous media. Journal of the Chemical Society, Perkin Transactions 1998;2:1857–64.

[10] Oakes J, Gratton P, Clark R, Wilkes I. Kinetic investigations of the oxidation of substituted arylazonaphthol dyes by hydrogen peroxide in alkaline solution. Journal of the Chemical Society, Perkin Transactions 1998;2: 2569–75.

[11] Oakes J, Gratton P. Kinetic investigations of the oxidation of Methyl Orange and substituted arylazonaphthol dyes by peracids in aqueous solution. Journal of the Chemical Society, Perkin Transactions 1998;2:2563–8.

[12] Oakes J, Gratton P. Kinetic investigation of the oxidation of arylazonaphthol dyes in hypochlorite solutions as a function of pH. Journal of the Chemical Society, Perkin Transactions 1998;2:2201–6.

[13] Bredereck K, Schumacher C. Structure reactivity correlations of azo reactive dyes based on H-acid. I. NMR chemical shift values, pK_a values, dyestuff aggregation, and dyeing behaviour. Dyes and Pigments 1993;21:23–43.

[14] Bredereck K, Schumacher C. Structure reactivity correlations of azo reactive dyes based on H-acid. II. Dye degradation by hypochlorite. Dyes and Pigments 1993;21: 45–66.

[15] Bredereck K, Schumacher C. Structure reactivity correlations of azo reactive dyes based on H-acid. III. Dye degradation by peroxide. Dyes and Pigments 1993;23:121–33.

[16] Bredereck K, Schumacher C. Structure reactivity correlations of azo reactive dyes based on H-acid. IV. Investigations into the light fastness in the dry state, in the wet state, and in the presence of perspiration. Dyes and Pigments 1993;23:135–47.

[17] Morley JO. Effect of molecular conformation on the electronic properties of donor-acceptor azobenzenes. Journal of the Chemical Society, Faraday Transaction 1995; 91(14):2067–9.

[18] Charlton MH, Docherty R, McGeein DJ, Morley JO. Theoretical investigation of the structure and spectra of donor-acceptor azobenzenes. Journal of the Chemical Society, Faraday Transaction 1993;89(11):1671–5.

[19] Maginn SJ, Bullock FJ, Docherty R. The solid state structures of donor-acceptor azobenzenes. Dyes and Pigments 1993;23:159–78.

[20] Malone JF, Andrews SJ, Bullock JF, Docherty R. The solid state structure of C.I. Disperse Orange 44. Dyes and Pigments 1996;30(3):183–200.

[21] Fagan PG, Roberts KJ, Docherty R. The crystallization of highly perfect metal-free phthalocyanine powders for "ab initio" structure solution by diffraction methods. Journal of Crystal Growth 1993;128(1-4):1257–62.

[22] Hammond RB, Roberts KJ, Docherty R, Edmondson M, Garins R. X-form metal-free phthalocyanine: crystal structure determination using a combination of high-resolution X-ray powder diffraction and molecular modeling techniques. Journal of the Chemical Society, Perkin Transaction 1996;2(8):1527–8.

[23] Fagan PG, Roberts KJ, Docherty R, Charlton AP, Potts GD, Jones W. The crystal structure of triphenodioxazine as solved by a new method utilizing high powder diffraction and computational chemistry techniques. Molecular Crystals and Liquid Crystals Science and Technology, Section A 1994;248:785–97.

[24] Fagan PG, Hammond RB, Roberts KJ, Docherty R, Charton AD, Jones W, Potts GD. An ab initio approach to crystal structure determination using high-resolution powder diffraction and computational chemistry techniques: application to 6,13-dichlorotripheno-dioxazine. Chemical Materials 1995;7(12):2322–6.

[25] Fukui K, Fujimoto H, editors. Frontier orbitals and reaction paths (selected papers of K. Fukui), World Scientific Series in 20th Century Chemistry vol. 7. Singapore: World Scientific; 1997.

[26] Flemming I. Frontier orbitals and organic chemical reactions. Chichester: Wiley-Interscience; 1976.

[27] Rauk A. Orbital interaction theory of organic chemistry. 2nd ed. New York: Wiley-Interscience; 2001.

[28] Hihara T, Okada Y, Morita Z. Azo-hydrazone tautomerism of phenylazo-naphthol sulfonates and their analysis using semiempirical molecular orbital PM5 method. Dyes and Pigment, accepted for publication.

[29] Stewart JJP. MOPAC 2002 and its manual. Tokyo: Fujitsu Ltd.; 2002.

[30] Sayage JA. Solvation and vibrational effects on proton tunneling in clusters. Faraday Discussions 1994;97:401–13.

[31] Lycka A. Multinuclear NMR of azo dyestuffs. Annual Reports on NMR Spectroscopy 1993;26:247–81.

[32] Fedorov LA. NMR spectroscopy of azo dyes. Russian Chemical Reviews 1988;57:941–55.

[33] Mustroph H. Über die azo-hydrazon-tautomerie. Zeitschrift fur Chemie 1987;27:281–9.

[34] Ball P, Nicholls CH. Azo-hydrazone tautomerism of hydroxyazo compounds. A review. Dyes and Pigments 1982;3:5–26.

[35] Kelemen J. Azo-hydrazone tautomerism in azo dyes. I. A comparative study of 1-phenylazo-2-naphthol and 1-phenylazo-2-naphtylamine derivatives by electronic spectroscopy. Dyes and Pigments 1981;2:73–91.

[36] Kelemen J. Azo-hydrazone tautomerism in azo dyes. II. Raman, NMR and mass spectrometric investigations of 1-phenylazo-2-naphtylamine and 1-phenylazo-2-naphthol and derivatives. Dyes and Pigments 1982;3:27–47.

[37] Bershtein IYA, Ginzburg OF. Tautomerism of aromatic azo-compounds. Russian Chemical Reviews 1972;41:97–110.

[38] Katritzky AR, Pozharskii AF. Handbook of heterocyclic chemistry. 2nd ed. Oxford: Pergamon/Elsevier Science; 2000.

[39] Katritzky AR, Marzin C, Linda P. The tautomerism of heterocycles, advances in heterocyclic chemistry, Supplement 1. New York: Academic Press; 1976.

[40] Elguero J, Katritzky AR, Denisko OV. Prototropic tautomerism of heterocycles: Heteroatomic tautomerism, General overview and methodology. Advances in Heterocyclic Chemistry 2000;76:1–84.

[41] Griffiths J. Prediction of colour change in dye equilibria. I. Azo and hydrazone tautomers and anions of 4-phenylazo-1-naphthols. Journal of the Dyers and Colourists 1972;88: 106–9.

[42] Fedorov LA, Sokolovskii SA. NMR titrations as a means for structural studies of organic analytical reagents based on the study of azo-quinone-hydrazone tautomerism by carbon-13 NMR spectroscopy. Zhurnal Analiticheskoi Khimii 1987;42(10):1753–61.

[43] Reeves RL, Kaiser RS. Selective solvation of hydrophobic ions in structured solvents. Azo-hydrazone tautomerism of azo dyes in aqueous organic solvents. Journal of Organic Chemistry 1970;35:3667–77.

[44] Bell SJ, Mazzola EP. ^{15}N NMR investigation of azo-hydrazone acid–base equilibria of FD&C Yellow No. 5 (Tartrazine) and two analogs. Dyes and Pigments 1989;11: 93–9.

[45] Mazzola EP, Bell SJ, Turujman SA, Barrows JN, Bailey Jr JE, McMahon JB, German TK, Reynolds WF. Nuclear magnetic resonance investigations of azo-hydrazone, acid–base equilibria of FD&C Yellow No. 5 tartrazine). Canadian Journal of Chemistry 1999;77:1941–5.

[46] Mazzola EP, Turujman SA, Bell SJ, Barrows JN, Bailey Jr JE, et al. Nuclear magnetic resonance investigation of azo-hydrazone, acid–base equilibria of FD&C Yellow No. 6. Tetrahedron 1996;52(16):5691–8.

[47] Tamura T, Kubozono T, Tamura M, Yoshimura H. Decoloration mechanism of dyes by bleaching agents. I. Analysis of reaction kinetics for dyes having a single phenolic hydroxyl group. Yukagaku 1995;14(12):1086–92 (Japanese)..

[48] Tamura T, Kubozono T, Tamura M, Yoshimura H. Decoloration mechanism of dyes by bleaching agents. II. Analysis of reaction kinetics for dyes having double phenolic hydroxyl group. Yukagaku 1995;14(12):1093–8 (Japanese)..

[49] Coen JJF, Smith AT, Candeias LP, Oakes J. New insight into mechanisms of dye degradation by one-electron oxidation processes. Journal of the Chemical Society, Perkin Transactions 2001;2:2125–9.

[50] Oakes J, Gratton P, Wilkes I, Gordon-Smith T. Kinetic and spectroscopic study of heterogeneous oxidation of azo dyes using hypochlorite. Coloration Technology 2001;117:76–81.

[51] Oakes J, Gratton P, Gordon-Smith T. Combined kinetic and spectroscopic study of oxidation of azo dyes in surfactant solutions by hypochlorite. Dyes and Pigments 2000;46:169–80.

[52] Oakes J. Photofading of textile dyes. Review of Coloration of Textiles and Related Topics 2001;31:21–8.

[53] Mekenyan O, Peitchev D, Bonchev D, Trinajstiæ N, Bangov I. Modelling the interactions of small organic molecules biomacromolecules, I. Interaction of substituted pyridines with anti-3-azopyridine antibody. Arzneimittel-Forschung/Drug Research 1986;36(I):176–83.

[54] Mekenyan O, Bonchev D, Trinajstiæ N, Peitchev D. Modelling the interactions of small organic molecules biomacromolecules, II. A generalized concept for biological interactions. Arzneimittel-Forschung/Drug Research 1986;36(I):421–4.

[55] Kikuchi O. Systematic QSAR procedures with quantum chemical descriptors. Quantitative Structure–Activity Relationship 1987;6:179–84.

[56] Schüürmann G. QSAR analysis of the acute fish toxicity of organic phosphorotionates using theoretically derived molecular descriptors. Environmental Toxicology and Chemistry 1990;9:417–28.

[57] Schüürmann G. Quatitative structure-property relationships for the polarizability, solvatochromic parameters and lipophilicity. Quantitative Structure–Activity Relationships 1990;9:326–33.

[58] CAChe 4.9, Reference Guide. Tokyo: Fujitsu Ltd, 2002.

[59] Klopman G. Chemical reactivity and the concept of charge- and frontier-controlled reactions. Journal of the American Chemical Society 1968;90:223–34.

[60] Hudson RF. The perturbation treatment of chemical reactivity. Angewandte Chemie, International Edition 1973;12:36–56.

[61] Klopman G. The control of chemical reactivity. Journal of Molecular Structure, THEOCHEM 1983;103:121–9.

[62] Houk KN. The frontier molecular orbital theory of cycloaddition reactions. Accounts of Chemical Research 1975;8:361–9.

[63] Houk KN, Munchausen LL. Ionization potentials, electron affinities, and reactivities of cycloalkenes and related electron-deficient alkenes. A frontier molecular orbital treatment of cycloalkene reactivities in cycloaddition, electrophilic, nucleophilic, and radical reactions. Journal of the American Chemical Society 1976;98:937–46.

[64] Folkes LK, Candeias LP, Wardman ?. Kinetics and mechanism of hypochlorous acid reactions. Archives of Biochemistry and Biophysics 1995;323(1):120–6.

[65] Klopman G, Tsuda K, Louis JB, Davis RE. Supernucleophiles I. The alpha effect. Tetrahedron 1970;26: 4549–54.

[66] Klopman G, Evans RC. Supernucleophiles II. Orbital interactions and nucleopholicity. Tetrahedron 1978;34: 269–73.

[67] Wolfe S, Mitchell DJ, Schlegel HB, Minot C, Eisenstein O. Theoretical studies of SN2 transition states, The alpha effect. Tetrahedron Letters 1982;23(6):615–8.

[68] Klopman G, Frierson MR. The alpha effect. A theoretical study incorporating solvent effect. Croatia Chemica Acta 1984;57(6):1411–5.

[69] DePuy CH, Della EW, Filley J, Grabowsky JJ, Bierbaum VM. Absence of an α-effect in the gas phase nucleophilic reactions of HOO^-. Journal of the American Chemical Society 1983;105:2481–2.

[70] Moiseev II. Hydrogen peroxide, water oxide and catalysis. Journal of Molecular Catalysis A: Chemical 1997;127:1–23.

[71] Chuang Y-Y, Truhlar DG. Geometry optimization with an infinite basis set. The Journal of Physical Chemistry A 1999;103(6):651–2.

[72] Wolfe S, Mitchell DJ, Schlegel HB, Minot C, Eisenstein O. Theoretical studies of SN2 transition states. The alpha effect. Tetrahedron Letters 1982;23:615–8.

[73] The Chemical Society of Japan. Chemical Handbook. 4th ed. Tokyo: Maruzen; 1975.

[74] Hihara T, Okada Y, Morita Z. Reaction of triphenodioxazine dyes with bleaching agents, hypochlorite and hydrogen peroxide, in aqueous solution. Dyes and Pigments 2000;46(3):181–92.

[75] Griffiths J, Hawkins C. The photochemical oxidation of 4-arylazo-1-naphthols. Journal of the Chemical Society Chemical, Communication 1972:463–4.

[76] Griffiths J, Hawkins C. Oxidation by singlet oxygen of arylazonaphthols exhibiting azo-hydrazone tautomerism. Journal of the Chemical Society, Perkin Transactions 1977;2:747–52.

[77] Morita Z, Hada S. A semiempirical molecular orbital study on the reaction of an aminopyrazolinyl azo dye with singlet molecular oxygen. Dyes and Pigments 1999;41(1): 1–10.

[78] Wasserman HH, Murray RW, editors. Singlet Oxygen. New York: Academic Press; 1979.

[79] Frimer AA, editor. Singlet O_2, vols. 1–4. Boca Raton: CRC Press; 1985.