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# Photocatalytic Degradation of Acid Azo Dyes in Aqueous $TiO_2$ Suspension

## I. The Effect of Substituents

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## *ABSTRACT*

*The effect of substituents on the photocatalytic degradation of H/K acid based azo dyes in aqueous solution is investigated. The intramolecular chemical environment can easily change the charge transfer direction of the conjugated pair on both sides of the trans-azobenzene backbone in* o-*arylazonaphthols. The contribution from an intramolecular hydrogen bond or* $O\text{–}H\cdots NH_2$ *hydrogen bond caused due to the pertinent substitution at the 1,8-positions in the naphthalene nucleus retards the attack of* $^1O_2$*, but the dyes could be destroyed by* $TiO_2$ *photoassisted catalysis. Compared with photosensitised degradation, homogeneous photocatalysis is a possible way of evaluating the light-fastness of azo dyes.* © *1998 Elsevier Science Ltd*

*Keywords*: acid azo dyes, photodegradation, $TiO_2$ substituents effect, photostability.

## INTRODUCTION

Acid azo dyes possess their color characteristics due to an intense electronic transition that produces a broad absorption spectrum in the visible region, and such dyes have found extensive use as wool dyes. Depending on their substituents, they vary widely in colour, in stability under UV radiation and in the strength of their adsorption on fibres.

It has been shown that the light fastness of dyes can be evaluated using kinetic parameters determined in liquid phase [1]. Kuramoto *et al.* [2] have studied substituent effects on the photofading of some naphthols in air-

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saturated methanol and observed that with the exception of the nitro group, the relative rate of photofading increased with the presence of electron-releasing substituents in the aryl ring. Matsui and co-workers [3] plotted the logarithm of the relative rates of aozonolysis of 1- (substituted phenylazo)-2-naphthols against the Hammett constants of the substituents. Sokolowska [4] noted that the presence of ortho electron-donating substituents decreased the rate of fading of aminazobenzenes, whereas in 3-amino-5-nitro (2, 1) benzisothiazole dyes, the influence was the opposite. All these experimental investigations dealt only with the influence of different substituents in the diazo components. Little data has been reported about the influence of the coupling component in naphthol azo dyes. We make an attempt to evaluate the correlation between the light fastness of H/K acid based azo dyes and the electronic effect of substituents both in the diazo and the coupling component. With the addition of a $TiO_2$ suspension, we have also studied the homogeneous photocatalytic degradation of the dyes, and found a new and rapid method for testing the light fastness of azo dyes.

## EXPERIMENTAL

### Preparation of $TiO_2$ suspension

A colloidal $TiO_2$ suspension was prepared via hydrolysis of $TiCl_4$ in aqueous solution [5]. The solution was passed through an ion exchanger in the $OH^-$ form [6]. A transparent $TiO_2$ solution was obtained, which had a sharp absorption band in the UV range (Fig. 1). The onset of this absorption (330 nm) corresponds to a band-gap of approximately $E^* = 3.3$ eV.

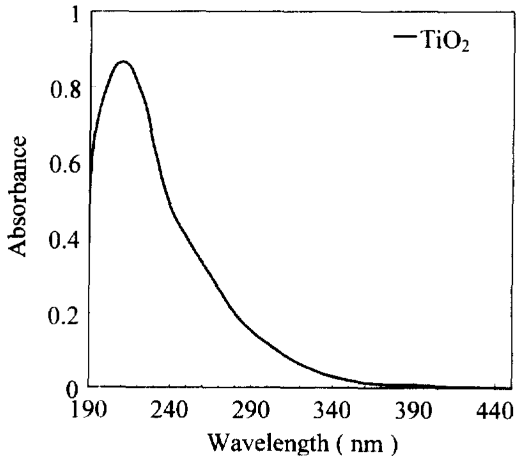
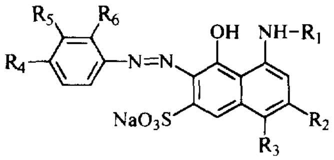


**Fig. 1.** Absorption spectrum of aqueous colloidal $TiO_2$ suspension used in this study.

**TABLE 1**
Dye Structures and Absorption Data in Aqueous Solutions



| *Dye* | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | $R_6$ | $\lambda_{max}$ *(nm)* | $\varepsilon(\times 10^{-4})$ *(l mol$^{-1}$ cm$^{-1}$)* |
|---|---|---|---|---|---|---|---|---|
| D-13 | COPh | H | $-SO_3Na$ | H | H | $-SO_3Na$ | 506.6 | 1.876 |
| D-25 | COPh | H | $-SO_3Na$ | H | H | $-NO_2$ | 514.8 | 1.538 |
| D-12 | COPh | $-SO_3Na$ | H | H | H | $-SO_3Na$ | 512.2 | 1.202 |
| D-16 | $COCH_3$ | $-SO_3Na$ | H | H | H | $-NO_2$ | 516.4 | 2.324 |
| D-23 | COPh | H | $-SO_3Na$ | $NO_2$ | H | $-NO_2$ | 518.2 | 1.739 |
| D-21 | COPh | $-SO_3Na$ | H | H | H | $-OCH_3$ | 523.8 | 2.231 |
| D-9 | $COCH_3$ | $-SO_3Na$ | H | H | H | $-OCH_3$ | 517.0 | 2.573 |
| D-8 | $COCH_3$ | $-SO_3Na$ | H | H | H | $-C-$ | 508.4 | 2.510 |
| D-11 | $SO_2Ph$ | $-SO_3Na$ | H | H | H | H | 506.6 | 8.447 |
| D-2 | H | $-SO_3Na$ | H | H | H | H | 527.2 | 2.473 |
| D-30 | $COCH_3$ | $SO_3Na$ | H | *p*-Cl-Ph-CO | H | H | 508.2 | 3.48 |
| D-19 | H | $-SO_3Na$ | H | H | H | $-OCH_3$ | 547.4 | 2.473 |
| D-10 | COPh | $-SO_3Na$ | H | $-NH-CO-CH_3$ | H | H | 522.0 | 1.839 |
| D-1 | COPh | $-SO_3Na$ | H | H | H | H | 508.8 | 1.792 |
| D4 | $COCH_3$ | $-SO_3Na$ | H | H | H | H | 505.2 | 2.621 |
| D-31 | COPh | $SO_3Na$ | H | *p*-Cl-Ph-CO | H | H | 508.2 | 3.167 |
| D-14 | COPh | $-SO_3Na$ | H | H | $-NH-CO-CH_3$ | H | 506.6 | 2.108 |
| D-29 | $SO_2Ph$ | $-SO_3Na$ | H | *p*-Cl-Ph-CO | H | H | 508.4 | 3.054 |
| D-24 | H | $-SO_3Na$ | H | $-NO_2$ | H | $-NO_2$ | 642.2 | 2.022 |
| D-5 | $COCH_3$ | $-SO_3Na$ | H | $-NO_2$ | H | H | 532.2 | 2.223 |
| D-20 | $COCH_3$ | $-SO_3Na$ | H | $-OCH_3$ | H | H | 524.2 | 2.741 |
| D-18 | $COCH_3$ | $-SO_3Na$ | H | $-SO_3Na$ | H | $-NO_2$ | 536.4 | 2.205 |
| D-27 | $COCH_3$ | $-SO_3Na$ | H | CN | H | H | 505.6 | 2.115 |
| D-28 | $COCH_3$ | $-SO_3Na$ | H | -O-Ph | H | H | 519.6 | 2.674 |
| D-22 | H | $-SO_3Na$ | H | $-OCH_3$ | H | H | 535.4 | 2.971 |
| D-7 | COPh | $-SO_3Na$ | H | H | $-NO_2$ | H | 499.4 | 1.819 |
| D-15 | $COCH_3$ | $-SO_3Na$ | H | H | $-NO_2$ | H | 501.2 | 1.785 |
| D-17 | $C_2H_5$ | $-SO_3Na$ | H | H | H | $-NO_2$ | 545.6 | 1.432 |
| D-6 | COPh | $-SO_3Na$ | H | H | H | $-NO_2$ | 519.6 | 1.347 |
| D-3 | COPh | $-SO_3Na$ | H | $-NO_2$ | H | H | 515.8 | 1.426 |

## Azo dyes

30 H/K acid derived azo dyes were synthesized and purified and their structures were confirmed by $^1$H NMR (Table 1). The concentration of the aqueous solutions of the dyes in the study was $2.5\times10^{-5}$ M.

## Experimental data

The aqueous borate or ammonium buffering solution (at pH 9.2) of $TiO_2$ used in the study was of concentration $2\times10^{-3}$ M. The dye degradation experiments were carried out using a photochemical reaction apparatus (British Applied Photophys. Limited) with a 200 W Hg lamp. Absorption spectra were measured on a UV-VIS spectrophotometer (Shimadzu UV-260) The photocatalytic degradation kinetic constants were given by the regression of analytical data and calibration with D-24 (660 nm).

## RESULTS AND DISCUSSION

### $TiO_2$ photocatalytic degradation of dyes

In aqueous solution, the photoassisted catalytic degradation of the dyes is caused by the active oxygen produced on the surface of $TiO_2$. The band-gap excitation of the *n*-type semiconductor $TiO_2$ colloid ($E_g = E_{CB} - E_{VB} = 3.2$ eV, $\lambda_{max} = 340$ nm) led to charge separation:

$$TiO_2 \xrightarrow{hv} (h^+_{VB} \cdots e^-_{CB}) \tag{1}$$

Photo-generated holes oxidized the pre-adsorbed $H_2O$ to generate $^{\cdot}OH$ free radicals, which are a powerful electrophilic oxidants.

$$H_2O + h^+_{VB} \rightarrow {}^{\cdot}OH + H^+ \tag{2}$$

The photogenerated electrons reduced the pre-adsorbed dissolved oxygen to produce superoxygen anionic free radical $O_2^{\cdot-}$

$$O_2 + e^-_{CB} \rightarrow O_2^{\cdot-} \tag{3}$$

Hydrazone-azo tautomerism of *o*-arylazonaphthols commonly exists, and it is believed that the photo-excitation oxidation of naphthol azo dyes is due to the reaction of the hydrazone tautomer with $^{\cdot}OH$ [7]. Kamat *et al.* [8] noted that the photocatalytic degradation rate of *o*-arylazonaphthol by $TiO_2$ compared very favorably with the reported results of hydroxyl radical-mediated degradation [7].

The intensity decrease of the 505–540 nm absorption band in Fig. 2 has been suggested to be due to the breakdown of the chromophore responsible for the characteristic colour of the azo dye. It is suggested that the site near

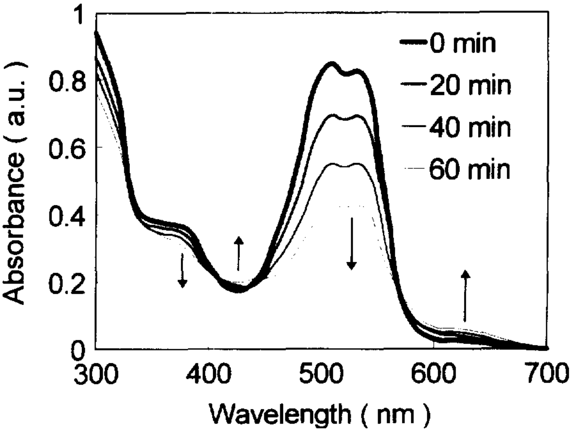


**Fig. 2.** Absorption spectra of aqueous D-8 solution recorded after different times of $TiO_2$ photocatalysis at pH 9.2.

the azo bond (C–N=N) is the target area in the $TiO_2$ photocatalytic degradation process. With the peak declining, the bands of the photo-products appeared around 425 nm and 580–680 nm and continued to rise during the period of irradiation. The parallel experiment on the $TiO_2$ photocatalytic degradation of these H/K acid derived azo dyes (Table 2) shows a correlation between the light-fastness of the dye and the substituents in the diazo component and coupling components. When the naphthalene nucleus is K acid, (dyes D-13, D-25, D-23) the $SO_3$ is substituent reduces the density of the electron cloud in the coupling component, which retards the attack of electrophilic singlet oxygen and results in the dyes having excellent stability. The existence of an intramolecular hydrogen bond [9, 10] in the above three dyes has been proved by the photosensitive degradation of these dyes in the ammonium buffering solution at pH 9.2 ($k_3$ shown in Table 2). The large ortho-$SO_3^-$ substituent in the diazo component of dyes D-13 and D-12 protects sterically the NHN = C group of the hydrazone form from the attack of $^1O_2$, besides forming an intramolecular hydrogen bond with the hydroxy group in the coupling component. The strong electron-acceptor *p*-$NO_2$ substituent on the phenyl ring in dye D-23 weakens the conjugative effect.

The rate of photochemical degradation with respect to the Hammett inductive constant $\sigma_1$ of substituents $R_1$ coupled with the amino-group in the naphthalene nucleus demonstrates that electron acceptor substituents $R_1$ can reduce the density of the electronic cloud in the naphthalene nucleus of *o*-arylazonaphthols, as shown in Table 3. When there is no electron acceptor substituent on the phenyl ring, the enhancement of intensity of the electron acceptor substituent strengthens the resonance effect and increases the resonance energy in the dye molecules ($R_6$=$OCH_3$ and H). When there is an

TABLE 2
Photosensitive $k_1$ and Photocatalytic $k_2$ Degradation Rates of the Dyes in Tetraborate Buffering Solution of pH 9.2 and Photosensitive Degradation Rate $k_3$ in Ammonium Buffering Solution of pH 9.2

| *Dyes* | $k_1(min^{-1}\times 10^4)$ | $k_2(min^{-1}\times 10^3)$ | *Fastness* | $k_3(min^{-1}\times 10^4)$ |
|---|---|---|---|---|
| D-13 | 0.12 | 3.396 | | 4.766[a] |
| D-25 | 2.28 | 2.58 | | 4.88[a] |
| D-12 | 3.84 | 3.76 | excellent | 8.70[a] |
| D-16 | 3.86 | 5.17 | | 9.78[a] |
| D-23 | 4.99 | 2.48 | | 24.2[a] |
| D-21 | 6.39 | 4.75 | | 7.71 |
| D-9 | 6.63 | 5.82 | | 9.31 |
| D-8 | 9.33 | 5.06 | | 13.2 |
| D-11 | 9.69 | 5.89 | | 15.63 |
| D-2 | 10.77 | 9.20 | | 29.0[a] |
| D-30 | 14.07 | 5.08 | | |
| D-19 | 15.52 | 8.78 | | 31.55[a] |
| D-10 | 16.04 | 5.90 | | 18.09 |
| D-1 | 17.73 | 6.43 | | 21.59 |
| D-4 | 26.57 | 6.73 | | 21.48 |
| D-31 | 19.73 | 6.00 | | |
| D-14 | 20.04 | 6.83 | | 23.2 |
| D-29 | 20.83 | 6.28 | | |
| D-24 | 21.02 | 6.086 | | 90.01 |
| D-5 | 21.15 | 6.31 | | 25.41 |
| D-20 | 23.21 | 6.82 | | |
| D-18 | 23.73 | 6.98 | | |
| D-27 | 26.97 | 7.94 | | |
| D-28 | 28.00 | 8.40 | | |
| D-22 | 29.55 | 10.74 | | 40.35 |
| D-7 | 29.85 | 8.78 | | 33.82 |
| D-15 | 31.72 | 10.83 | | 26.88 |
| D-17 | 85.55 | 19.08 | | 53.39 |
| D-6 | 134.5 | 22.36 | bad | 72.29 |
| D-3 | 215.5 | 28.83 | | 185.2 |

[a] Because organic compounds can form hydrogen bonds with amines [11], the intramolecular hydrogen bond in *o*-arylazonaphthols is destroyed and it is easy to be attacked by the electrophilic oxidant.

electron acceptor substituent on the phenyl ring, the strong electron acceptor substituent weakens the resonance effect ($R_4$=*p*-Cl-Ph-CO). Owing to the effect of the position in the naphthalene nucleus, the O–H· · ·$NH_2$ hydrogen bond distributes the electronic cloud well, and makes dye D-2 stable. The data (Table 2) on the photosensitive degradation of D-2 and D-19 in different buffering solutions also show, the existence of the O–H· · ·$NH_2$ hydrogen bond.

The intramolecular resonance energy in the conjugated molecules of *o*-arylazonaphthols determines the light fastness of the dyes. The intramolecular chemical environment can easily change the charge transfer direction of the conjugated pair on the two sides of the trans-azobenzene backbone in *o*-arylazonaphthols, as shown in Fig. 3. The electron attracting benzoyl substituent, coupled with the amino group, lowers the density of the electron

TABLE 3
Correlation Between the Inductive Effect of Substituents ($R_1$) and the Rate of Photosensitive as well as $TiO_2$-Photocatalytic Degradation of the Dyes at pH 9.2

| *Dyes* | $R_1$ | $\sigma$ | $k_1(min^{-1}\times 10^4)$ | $k_2(min^{-1}\times 10^4)$ |
|---|---|---|---|---|
| D-11 | $SO_2Ph$ | 0.495 | 9.69 | 5.89 |
| D-1 | COPh | 0.42 | 17.73 | 6.43 |
| D-4 | $COCH_3$ | 0.40 | 26.57 | 6.73 |
| D-2 | H | 0 | 10.77 | 9.20 |
| D-30 | $COCH_3$ | 0.40 | 14.07 | 5.08 |
| D-31 | COPh | 0.42 | 19.73 | 6.00 |
| D-29 | $SO_2Ph$ | 0.495 | 20.83 | 6.28 |
| D-21 | COPh | 0.42 | 6.39 | 4.75 |
| D-9 | $COCH_3$ | 0.40 | 6.63 | 5.82 |
| D-19 | H | 0 | 15.52 | 8.78 |

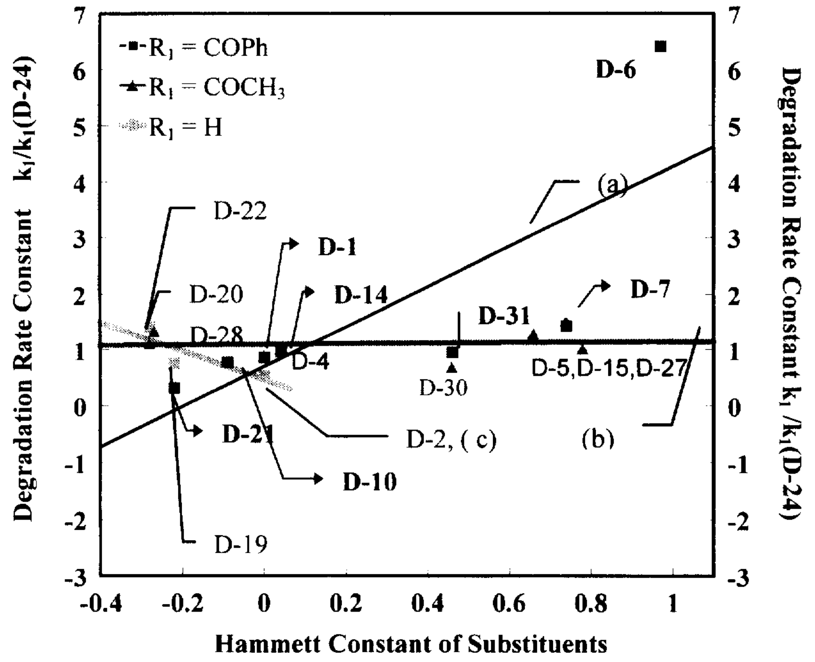


**Fig. 3.** Relationship between electronic effect of substituents and the rate of photosensitive degradation of dyes (relative to D-24) at pH 9.2. Line (a): $R_1$ = COPh; line (b): $R_1 = COCH_3$; line (c): $R_1$ = H.

cloud in the coupling component, and therefore an electron-donating (substituent in the diazo component promotes the conjugation. On the contrary, when a strong electron donor group, e.g. $NH_2$, is in the naphthalene nucleus, an electron donor substituent in the diazo component is unfavorable for the resonance of the conjugated pair. However, dye D-17 is an exception. Probably, the stronger electron donor $NHC_2H_5$ group increases the density of the electron cloud in the naphthalene nucleus and makes dye D-17 more readily attacked by $^1O_2$ or the electrophilic $^{\bullet}OH$ radical. Since the electronic effect of the electron attracting $COCH_3$ substituents lies between that of COPh and H, it is unclear whether substituent in the diazo component contribute to the conjugate system of the dye.

## CONCLUSIONS

The photocatalytic degradation of H/K acid derived azo dyes in aqueous $TiO_2$ suspension follows apparent first-order kinetics. $TiO_2$ acts as a strong photosensitizer for $^{\bullet}OH$, $^{\bullet}OOH$ and $O_2^{\bullet -}$ radicals which are highly reactive towards azo dyes. The intramolecular resonance energy in the conjugated molecules of *o*-arylazonaphthols determines the light fastness of the dyes. The intramolecular chemical environment can easily change the charge transfer direction of the conjugated pair in both sides of the trans-azobenzene backbone in *o*-arylazonaphthols. The contribution from an intramolecular hydrogen bond or $O\text{-}H\cdots NH_2$ hydrogen bond caused by the effect of its position in the naphthalene nucleus retards the attack of $^1O_2$, but dyes could be destroyed by $TiO_2$ photoassisted catalysis. Comparing with the photosensitive degradation, the homogeneous photocatalysis is a possible way of testing the light-fastness of azo dyes.

## ACKNOWLEDGEMENTS

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