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Dyes and Pigments 61 (2004) 63–67
DYES and PIGMENTS
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Hydroxide-catalysed decomposition of benzoquinone-imine dyes

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Received 29 July 2003; received in revised form 16 September 2003; accepted 22 September 2003

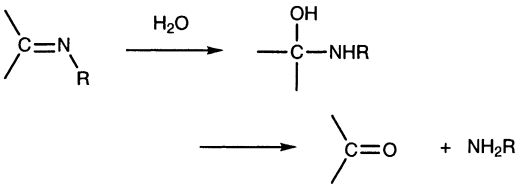
Abstract

A comparative kinetic study of the hydroxide-catalysed decomposition of benzoquinone-imine dyes such as 4-[(4-hydroxyphenyl)imino]-2,5-cyclohexadien-1-one (indophenol, **IP**), 2,6-dichloro-4-[(4-hydroxyphenyl)imino]-2,5-cyclohexadien-1-one (**DCIP**), 2,6-dibromo-4-[(4-hydroxyphenyl)imino]-2,5-cyclohexadien-1-one (**DBIP**), and 2,6-dibromo-4-[(4-hydroxy-3-methoxyphenyl)imino]-2,5-cyclohexadien-1-one (**DBMIP**) was carried out. The kinetic data are consistent with nucleophilic addition of hydroxide anions to the imine carbon (step 1), followed by cleavage of the resulting carbinolamine intermediate (step 2). The reactivity for step 1 increases in the order **IP** < **DCIP** < **DBIP** < **DBMIP**, whereas the reactivity order for step 2 is **DBIP** < **DCIP** < **DBMIP** < **IP**. Application of the Hammett equation to the rate values corresponding to **IP**, **DCIP** and **DBIP** renders ρ values of (0.72 ± 0.01) and (-0.46 ± 0.03) for steps 1 and 2, respectively.

Keywords: Benzoquinone-imine dyes; Indophenols; Hydrolysis; Hammett equation; Linear free-energy relationship

1. Introduction

Quinone-imine dyes are among the most important industrial dyestuffs, and many of these dyes are also frequently used in analytical chemistry as redox, acid-base, adsorption, and solvent polarity indicators [1,2]. The ease with which the imine functionality of quinone-imine dyes can hydrolyze, however, limits the applications of these dyes. The general mechanism for hydrolysis of an imine group involves addition of water to the imine carbon followed by elimination of the nitrogen moiety from a tetrahedral (carbinolamine) intermediate, as shown in Eq. (1) [3].



(1)

Despite the numerous kinetic studies on hydrolytic decomposition of carbon-nitrogen double bond containing compounds, very limited quantitative data are indeed available for quinone-imine dyes such as indophenol (i.e., 4-[(4-hydroxyphenyl)imino]-2,5-cyclohexadien-1-one) and its derivatives [4–8]. In the present paper, a kinetic

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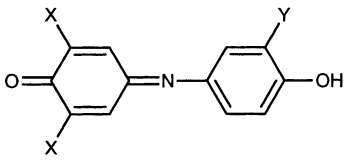
doi:10.1016/j.dyepig.2003.09.001

study on the hydroxide-catalysed decomposition of a series of structurally related benzoquinone-imine dyes (Chart 1) is presented. Substrate reactivity is discussed in the context of Eq. (1), and interpreted in terms of the corresponding substituent electronic effect.

2. Results and discussion

The hydrolytic decomposition of the benzoquinone-imine dyes shown in Chart 1 was carried in aqueous solutions having varying NaOH concentration (from 0.1 to 0.5 M). Under these experimental conditions, the benzoquinone-imine dyes exist predominantly under their anionic forms ($pK_{a3} = 8.2$ (**IP**), 5.8 (**DCIP** and **DBIP**) [9]); thus, the corresponding visible absorption spectra are characterized by an intense absorption band centered in the 590–630 nm region (λ_{max}, Table 1). When the intensity of this visible band is monitored as a function of time, the depletion of such signal is observed (Fig. 1 is representative). Interestingly, the initial time resolved absorption spectra show a well-defined isosbestic point (Fig. 1A) in the 495–545 nm region (λ_{iso}, Table 1), which on longer time scales is no longer observed since depletion takes place throughout the entire visible region (Fig. 1B). In all cases, a hypsochromic shift of the wavelength of maximum absorption also becomes noticeable as the depletion progresses (Fig. 1B). UV–visible and ^{1}H-NMR investigations clearly indicate that the overall spectral changes are due to the fact that the benzoquinone-imine dyes being studied are first hydrolyzed into their corresponding 1,4-aromatic quinone and 4-ami-



Dye	X	Y
IP	H	H
DCIP	Cl	H
DBIP	Br	H
DBMIP	Br	CH_3O

Chart 1.

Table 1
Spectral parameters and rate constants for hydrolysis of benzoquinone-imine dyes in NaOH aqueous solutions[a]

Dye	λ_{max}[b] (nm)	λ_{iso}[c] (nm)	k_1 (10^{-4} M^{-1} s^{-1})	k_2 (10^{-5} s^{-1})
IP	629	542	2.36±0.02	8.7±0.2
DCIP	602	536	8.17±0.08	4.1±0.1
DBIP	606	535	8.8±0.2	3.6±0.1
DBMIP	591	496	20.2±0.2	5.2±0.1

[a] $T = (25.0 \pm 0.1)$ °C; $\mu = 1$ M (NaCl).
[b] Wavelength of maximun absorption.
[c] Isosbestic point.

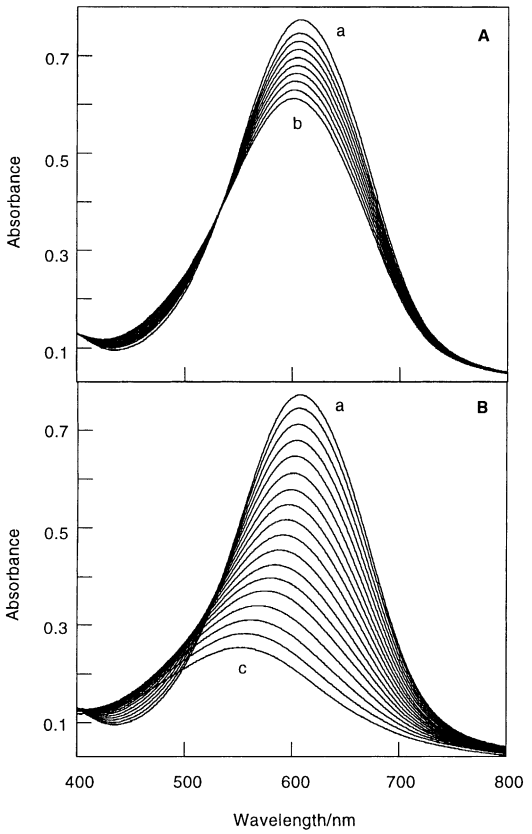


Fig. 1. Time resolved absorption spectra for **DBIP** in 0.01 M NaOH aqueous solution obtained within 1 min and (A) 80 min (from a to b), and (B) 480 min (from a to c) after sample preparation.

nophenol, in agreement with literature reports [6,10].

As it can be inferred from Fig. 1, the shape of the kinetic traces varies with monitoring wavelength (λ). For instance, at λ longer than that corresponding to the isosbestic point a decay signal is observed. Kinetic traces recorded at λ longer than ca. 680 nm follow first-order kinetics up to at least three half-lives (Fig. 2 inset is representative), and the resulting observed rate constant values (independent of λ) show a linear correlation with NaOH concentration (Fig. 3). When monitoring at shorter wavelengths (i.e., $\lambda_{iso} < \lambda < 680$ nm), the shorter the wavelength, the poorer the overall first-order fitting, and the lower the resulting observed rate constant. On the other hand, at λ shorter than λ_{iso} a growth followed by a decay is detected (Fig. 2 is representative). Depending on the substrate employed, the rate for the growth and decay processes may be quite close; therefore a precise evaluation of the corresponding rate constants becomes difficult. However, when kinetic traces of the type shown in Fig. 2 are fitted to a double exponential function, it is found that the larger rate constant (i.e., growth process) agrees excellently with the value determined from the corresponding decay signal collected at $\lambda >$ 680 nm. Thus, rate constants determined at $\lambda >$ 680 nm were employed as (fixed) parameters in the double exponential function used to find the rate constants corresponding to the (slower) decay process monitored at $\lambda < \lambda_{iso}$. Resulting values are found to be essentially independent of NaOH concentration (Fig. 4).[1]

The kinetic data displayed in Figs. 1 and 2 are fully consistent with the general mechanism shown

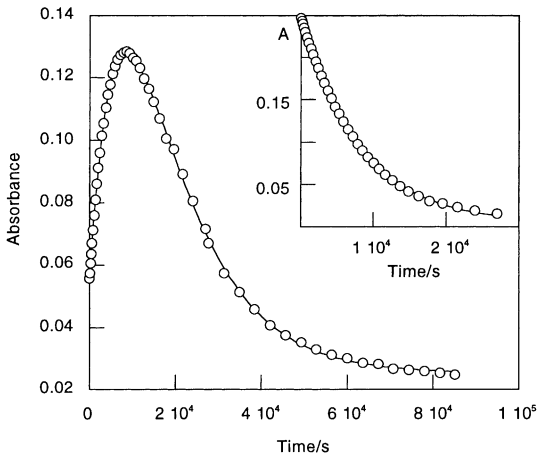


Fig. 2. Kinetic trace monitored at 470 nm for **IP** decomposition in 0.05 M NaOH aqueous solution. Inset: kinetic trace monitored at 700 nm.

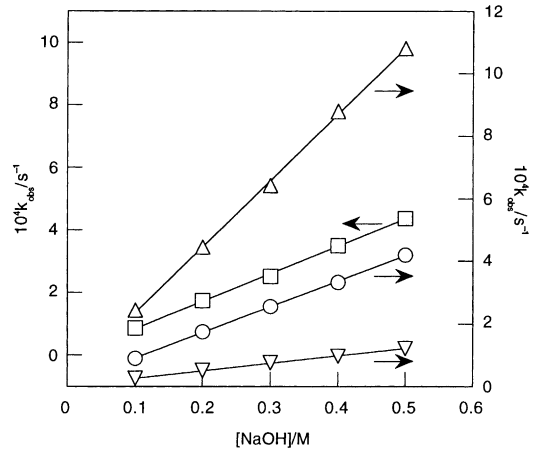


Fig. 3. Plot of observed rate constants (corresponding to decay traces recorded at $\lambda >$ 680 nm) vs. NaOH concentration for hydrolytic decomposition of **IP** (▽), **DCIP** (○), **DBIP** (□), and **DBMIP** (△) in aqueous solution.

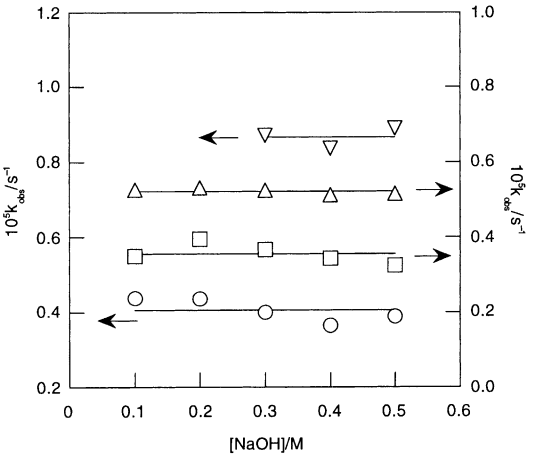


Fig. 4. Plot of observed rate constants (corresponding to the decay of traces recorded at $\lambda < \lambda_{iso}$) vs. NaOH concentration for hydrolytic decomposition of **IP** (▽), **DCIP** (○), **DBIP** (□), and **DBMIP** (△) in aqueous solution [11].

[1] Values for **IP** at 0.01 and 0.02 M could not be determined as the amplitude for the corresponding growth/decay signal is too small to carry out kinetic measurements.

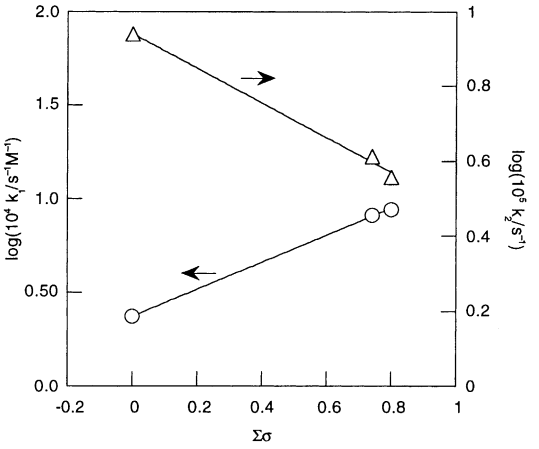


Fig. 5. Hammett plot for formation (○) and dissociation (△) of the carbinolamine intermediate involved in the decomposition of indophenol (**IP**) and its derivatives (**DCIP** and **DBIP**) in NaOH aqueous solution.

in Eq. (1). Thus, the (fast) decay monitored at $\lambda >$ 680 nm and growth signal recorded at $\lambda < \lambda_{iso}$ render rate constant values for step 1, i.e., conversion of the quinone-imine dye into the carbinolamine intermediate upon addition of hydroxide anions to the imine carbon. As already mentioned, the resulting observed rate constants for the traces just described are found to be directly proportional to the concentration of hydroxide anions (Fig. 3). The corresponding second-order rate constants (k_1, Table 1) are found to increase in the order **IP** < **DCIP** < **DBIP** < **DBMIP**. This reactivity order can be easily explained in terms of the electronic character of the substituents on the quinoid and phenolic rings. As the ability of the substituents to withdraw electrons increases, so does the electrophilic character of the imine carbon, and consequently, the rate of addition of hydroxide anions. Indeed, application of the Hammett equation to the rate values corresponding to **IP**, **DCIP**, and **DBIP** renders a linear plot (Fig. 5) characterized by a ρ_1 value of (0.72 ± 0.01). Likewise, the (slow) decay monitored following the growth at $\lambda < \lambda_{iso}$ renders rate constant values for step 2, i.e., decomposition of the carbinolamine intermediate. The corresponding NaOH-independent rate values (k_2, Table 1) increase in the order **DBIP** < **DCIP** < **DBMIP** < **IP** This reactivity order can also be easily explained in terms of the electronic character of the substituents on the quinoid and phenolic rings. As the electron-withdrawing character of the substituents on the quinoid ring increases, so does the strength of the C–N bond, and consequently, the rate of C–N bond dissociation is expected to decrease. Application of the Hammett equation to the rate values corresponding to **IP**, **DCIP** and **DBIP** renders a linear plot (Fig. 5) characterized by a ρ_2 value of (-0.46 ± 0.03). On the contrary, as the electron-withdrawing character of the substituents on the phenolic ring increases, so does the leaving group ability of N, and consequently, the rate of C–N bond dissociation is expected to increase. Although the number of experimental data for substitution at the phenolic ring is indeed quite limited, comparison of the rate values for **DBIP** and **DBMIP** leads to estimated ρ values of 3.6 and 1.6 for steps 1 and 2, respectively. Interestingly, these values would suggest that the susceptibility of the two processes controlling dye decomposition (i.e., formation and dissociation of the carbinolamine intermediate) to electrical effects at the phenolic ring is more pronounced than that at the quinoid ring (which in turn is consistent with the extended π-conjugation between the *N*-aryl fragment and the imine group).

In summary, rate (k) and reaction (ρ) constants for hydroxide-catalyzed decomposition of a series of structurally related benzoquinone-imine dyes are reported. These values should prove valuable to the use of benzoquinone-imine dyes in analytical chemistry applications requiring alkaline conditions, such as in modified electrodes [11] for example.

3. Experimental

4-[(4-Hydroxyphenyl)imino]-2,5-cyclohexadien-1-one (sodium salt, Aldrich) and 2,6-dibromo-4-[(4-hydroxyphenyl)imino]-2,5-cyclohexadien-1-one (TCI) were used as received; 2,6-dichloro-4-[(4-hydroxyphenyl)imino] - 2,5 - cyclohexadien - 1 - one and 2,6-dibromo-4-[(4-hydroxy-3-methoxyphenyl)-imino]-2,5-cyclohexadien-1-one (TCI) were purified by column chromatography on silica gel using ethyl acetate:cyclohexane (1:3) as eluent.

The purity and identity of all four dyes were checked by TLC and ^{1}H-NMR spectroscopy (using a Bruker Model AM-300 NMR spectrometer). Aqueous solutions were prepared using analytical grade reagents (BDH) and water purified by passage through a Millipore apparatus.

The hydrolysis of quinone-imine dyes in NaOH aqueous solutions was monitored spectrophotometrically using a Varian Cary 1 Bio spectrophotometer with a thermostated cell compartment connected to a heated/refrigerated circulating bath (VWR Canlab Model 1160A). Reactions were initiated by adding the substrate (dissolved in water) to a solution containing all the other constituents. Typical dye concentrations were in the order of $3–5\times10^{-5}$ M. All reactions were carried out under pseudo-first order conditions and followed until at least 80–90% conversion of the starting material was observed. The ionic strength of the solutions was kept constant at 1 M using NaCl as compensating electrolyte. All measurements were carried out at $(25.0\pm0.1)^{\circ}$C. Kinetic traces were obtained by monitoring either the disappearance of the quinone-imine dye (i.e., λ ca. 700 nm in the cases of **IP** and **DBIP**, and 686 nm in the cases of **DCIP** and **DBMIP**) or the formation/disappearance of the intermediate carbinolamine (i.e., λ ca. 470, 451, 470 and 440 nm for **IP**, **DCIP**, **DBIP** and **DBMIP**, respectively). Values for the observed rate constants were then obtained by fitting the kinetic traces to either a single or double exponential function by using the general curve fitting procedure of Kaleidagraph software (version 3.0.5) from Abelbeck Software. All observed rate constants values correspond to the average of at least two independent kinetic runs.

Acknowledgements

Financial support from the Natural Sciences and Engineering Research Council (NSERC) of Canada is gratefully acknowledged.

References

[1] Ottaway JM. In: Bishop E, editor. Indicators. Pergamon Press; 1972 [chapter 8A].
[2] Reichardt C. Solvents and solvent effects in organic chemistry. Weinheim: VCH; 1990 [chapter 6].
[3] March J. Advanced organic chemistry. New York: John Wiley & Sons; 1992. p. 884–5 [and references therein].
[4] Cohen B, Phillips M. Public Health Reports (US), Supplement 1929;74:1–33.
[5] Buschmann H-J, Schollmeyer E. J Inclusion Phenom Mol Recognit Chem 1992;14:91–9.
[6] Lange R, Friebe R, Linow F. Die Nahrung 1980;24:907–21.
[7] Brown KC, Corbett JF. J Chem Soc Perkin Trans 2 1981: 886–9.
[8] Barra M, Croll LM, Tan A, Tao W. Dyes and Pigments 2002;53:137–42.
[9] Patrick A, Svehla G. Anal Chim Acta 1977;88:363–70.
[10] Reeves RL, Tong LKJ. J Org Chem 1965;30:237–42.
[11] Florou AB, Prodromidis MI, Karayannis MI, Tzouwara-Karayanni SM. Electroanalysis 2000;12:361–8.