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Dyes and Pigments 53 (2002) 137–142

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Kinetic studies on the proton-catalysed hydrolytic decomposition of quinone-imine dyes

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Received 5 November 2001; received in revised form 17 January 2002; accepted 18 January 2002

Abstract

Kinetic studies on the hydrolytic decomposition of 4-[[4-(dimethylamino)phenyl]imino]-2,5-cyclohexadien-1-one [phenol blue (PB)], 4-[(4-hydroxyphenyl)imino]-2,5-cyclohexadien-1-one [indophenol (IP)], and 4-[[4-(dimethylamino)-phenyl]imino]-naphthalen-1-one [indophenol blue, (IPB)] in HCl solutions are consistent with nucleophilic addition of water to the protonated imine functionality. The reactivity increases in the order $PB \sim IP < IPB$, which is attributed to resonance effects. Interestingly, in the case of PB and IPB the reaction is inhibited as the polarity of the solvent decreases, whereas in the case of IP the hydrolytic decomposition is accelerated. These inverse trends are interpreted in terms of the opposite changes in dipole moment associated with each type of system (i.e. PB/IPB vs. IP).

Keywords: Quinone-imine dyes; Phenol blue; Indophenol; Indophenol blue; Hydrolysis; Solvent effects

1. Introduction

Quinone-imine dyes such as 4-[[4-(dimethylamino)phenyl]imino]-2,5-cyclohexadien-1-one [phenol blue (PB)], 4-[(4-hydroxyphenyl)imino]-2,5-cyclohexadien-1-one [indophenol (IP)], and 4-[[4-(dimethylamino)phenyl]imino]-naphthalen-1-one [indophenol blue (IPB)] are commonly used as redox indicators [1] as well as solvent polarity indicators [2]. Applications of these dyes, however, are limited by the fact that quinone-imine dyes are unstable under acidic and basic solutions [1]. Compounds containing an imine group are fairly reactive in the presence of nucleophilic reagents, and are known to easily undergo hydrolysis [3]. The general mechanism for hydrolysis of carbon-nitrogen double bonds involves addition of water to the carbon atom followed by elimination of the nitrogen moiety from a tetrahedral intermediate, yielding a ketone (or aldehyde) and an amine as shown in Eq. (1) [4]. In fact, it has been reported that PB hydrolyses in acidic aqueous solution to 1,4-benzoquinone and *N*,*N*-dimethyl-*p*-phenylenediamine [5,6], while IP has been shown to be first hydrolyzed in alkaline solutions into 1,4-benzoquinone and 4-aminophenol [7]. The study of these reactions, however, has been for the most part only qualitative; to the best of our knowledge, very limited data on the reactivity of the above mentioned quinone-imine dyes in aqueous media are indeed available [6,7].

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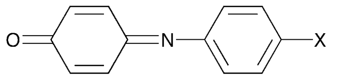
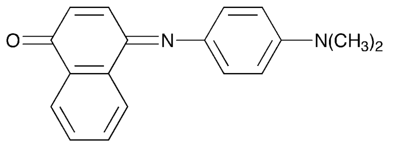
PII: S0143-7208(02)00013-X

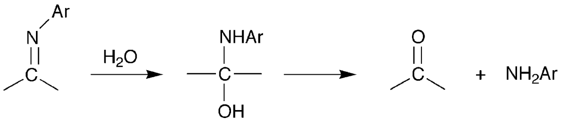


PB X = N(CH$_3$)$_2$
IP X = OH



IPB

In the present paper, a kinetic study on the proton-catalysed hydrolysis of PB, IP and IPB is described. The importance of solvent polarity on these reactions is also presented.



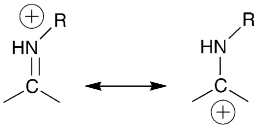
(1)

2. Results and discussion

The hydrolytic decomposition of quinone-imine dyes PB, IP and IPB was studied in water and in dioxane/water solutions at pHs ranging from 0.5 to 2. In the case of IPB, and due to its low solubility in water, kinetic studies were carried out in dioxane/water solutions only.

Under the experimental conditions of this work, IP exists in its neutral form (pK_{a3} = 8.1) [8], whereas PB and IPB (pK_{a3} = 4.8) [8, 9] exist in their cationic (ammonium) forms. When the intensity corresponding to the visible absorption band of PB, IP or IPB in aqueous solutions at pH < 2 (i.e. λ_{max} ca. 570, 495 and 430 nm, respectively) is monitored as a function of time, the disappearance or 'bleaching' of such signal is observed (Fig. 1 is representative). ^{1}H NMR investigations clearly indicate that this bleaching is due to the fact that the quinone-imine dyes being studied are completely hydrolyzed into the corresponding 1,4-aromatic quinone and *N*,*N*-dimethyl-*p*-phenylenediamine (PB and IPB) or 4-aminophenol (IP), in agreement with reports in the literature [5–7]

In all cases, the rate of hydrolytic decomposition follows first-order kinetics and it is found to increase as proton concentration also increases. This observation is in agreement with the fact that, under acidic conditions, the addition of water to an imine group is facilitated as the result of protonation of the nitrogen atom and concomitant increase in the electrophilic character of the imine carbon atom as shown in Eq. (2) [4].



(2)

In the case of PB and IP, plots of the observed rate constant (k_{obs}) as a function of proton concentration are non-linear (Figs. 2 and 3), while in the case of IPB, k_{obs} is found to be directly proportional to proton concentration (Fig. 4). Furthermore, it is interesting to notice that while k_{obs} values for PB and IPB decrease with decreasing solvent polarity, the opposite trend is observed in the case of IP.

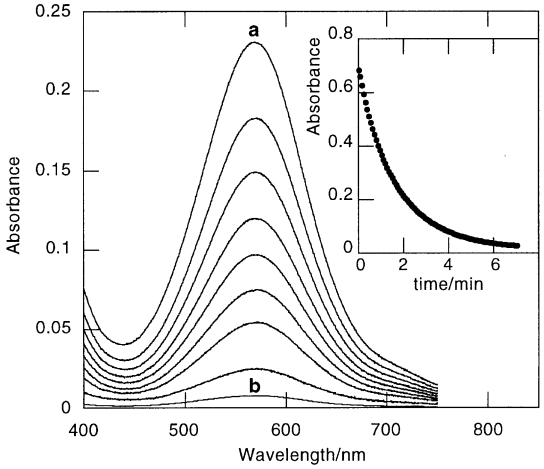


Fig. 1. Time-resolved absorption spectra for PB decomposition in 0.103 M HCl aqueous solution, obtained within 1 min. and 20 min. (from a to b) after sample preparation. Inset: kinetic trace (monitored at 495 nm) for IP decomposition in 43 mM HCl in 30:70 (v/v) dioxane/water solution.

The kinetic data displayed in Figs. 2 to 4 can be interpreted in terms of the reaction mechanism shown in Scheme 1. The corresponding expression for the observed rate constant is given by Eq. (3), where K_a and $k_{\text{hydrolysis}}$ represent, respectively, the acid dissociation equilibrium constant (express in terms of concentration) and the experimental first-order rate constant for hydrolysis of the protonated imine moiety.

$$k_{\text{obs}} = \frac{k_{\text{hydrolysis}}[\text{H}^+]}{[\text{H}^+] + K_a} \tag{3}$$

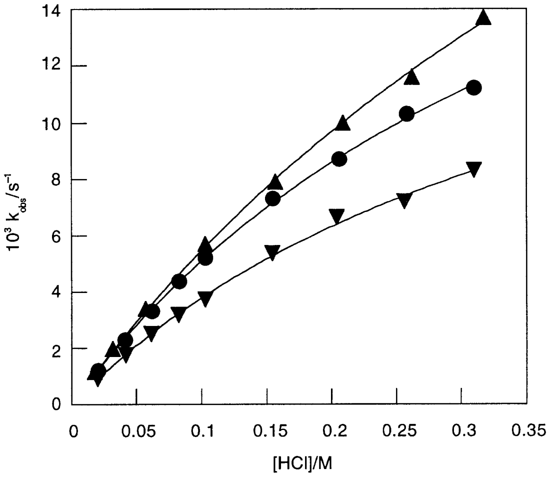


Fig. 2. Plot of observed rate constants vs. HCl concentration for hydrolytic decomposition of PB in water (▲), in 20:80 (v/v) dioxane/water (●) and in 30:70 (v/v) dioxane/water (▼) solutions.

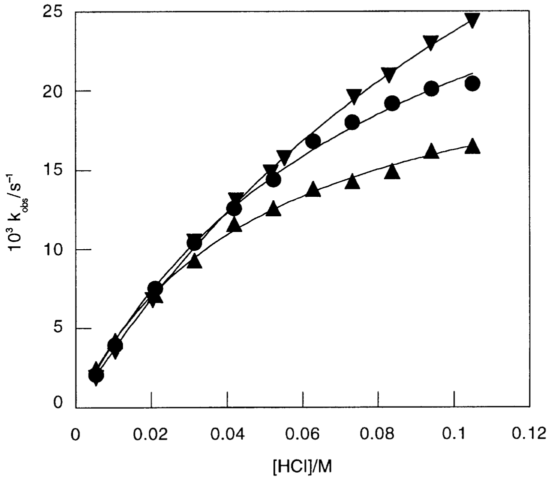


Fig. 3. Plot of observed rate constants vs. HCl concentration for hydrolytic decomposition of IP in water (▲), in 20:80 (v/v) dioxane/water (●) and in 30:70 (v/v) dioxane/water (▼) solutions.

In all cases, the independent terms corresponding to the k_{obs} vs. $[\text{H}^+]$ plots are negligible (i.e., under the experimental conditions of this work, the rate of hydrolysis of the unprotonated imine moiety is negligible with respect to that of its conjugate acid). Non-linear fittings of k_{obs} vs. $[\text{H}^+]$ data for PB and IP according to Eq. (3) lead to the values of K_a and $k_{\text{hydrolysis}}$ summarized in Table 1. While a non-linear fitting is preferred, it should be pointed out here that the corresponding double reciprocal plots for both substrates are indeed linear (Figs. 5 and 6), which is fully consistent with

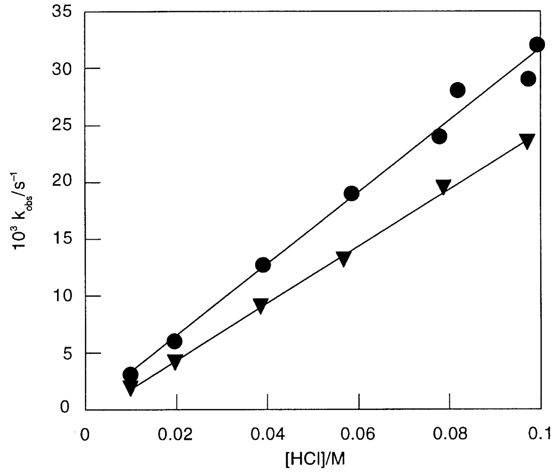
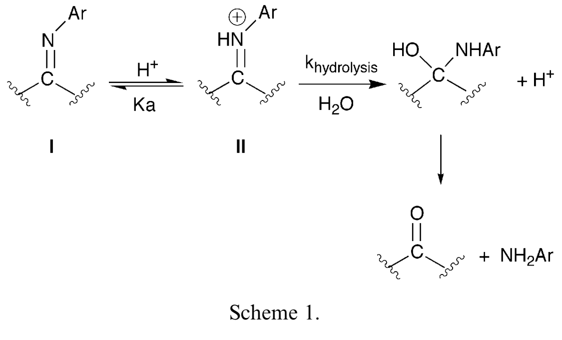


Fig. 4. Plot of observed rate constants vs. HCl concentration for hydrolytic decomposition of IPB in 20:80 (v/v) (●) and 30:70 (v/v) (▼) dioxane/water solutions.



Scheme 1.

Eq. (3). Furthermore, the values of K_a and $k_{hydrolysis}$ obtained from the corresponding slopes and intercepts (not shown) are in excellent agreement with those listed in Table 1. On the other hand, the linear dependence observed between k_{obs} values for IPB and proton concentration would indicate that, under the experimental conditions of this work, K_a is at least ten times larger than the highest proton concentration used (i.e., $K_a \geqslant 1$ M); thus, the slope of the linear plots shown in Fig. 4 corresponds to the ratio $k_{hydrolysis}/K_a$ (Table 1).

Table 1

Acid dissociation equilibrium constants and first-order rate constants for hydrolysis of quinone–imine dyes in aqueous solutions[a]

Dye	% Dioxane	$k_{hydrolysis}$ (s^{-1})	K_a (M)
PB	0	(0.042±0.003)	(0.66±0.06)
	20	(0.027±0.001)	(0.43±0.03)
	30	(0.019±0.001)	(0.41±0.04)
IP	0	(0.024±0.001)	(0.049±0.003)
	20	(0.037±0.001)	(0.081±0.006)
	30	(0.062±0.002)	(0.161±0.009)
IPB	20	(0.317±0.006)[b]	>1
	30	(0.243±0.004)[b]	>1

[a] $T = 25$ °C; $\mu = 0.5$ M (NaCl).

[b] ($k_{hydrolysis} \times Ka^{-1}$)/$M^{-1}$ s^{-1} value, see text.

In the case of PB, the resulting $k_{hydrolysis}/K_a$ value in water (i.e., 6.36×10^{-2} M^{-1} s^{-1}) is in good agreement with the reported second-order catalytic rate constant for proton, namely 3.51×10^{-2} M^{-1} s^{-1}, determined in aqueous solution at 25 °C (ionic strength not specified) [6]. Furthermore, the K_a value obtained for IP in water is comparable to the second dissociation acidity constant reported in the literature at 25 °C, i.e. $pK_{a2} = 0.95$ [8].

Examination of the values given in Table 1 shows clear substituent effects. Comparison of the $k_{hydrolysis}$ values shows that substrate reactivity increases in the order PB ~ IP < IPB. This result is in good agreement with the higher reactivity generally observed for naphthyl vs. phenyl derivatives as a result of resonance stabilization. On the other hand, K_a values are found to increase in the order IP < PB < IPB. This result can be easily explained in terms of (i) the electronic character of the aryl group attached to the imine nitrogen, and (ii) resonance effects. The (strong) electron-withdrawing effect of the 4-$(CH_3)_2NH^+$ group (IPB and PB) when compared with the overall electron-donating character of the 4-HO group (IP) would render the imine moiety of IPB and PB more acidic than that of IP. On the other hand, resonance stabilization at the imine carbon ring would cause the imine moiety of IPB to be more acidic

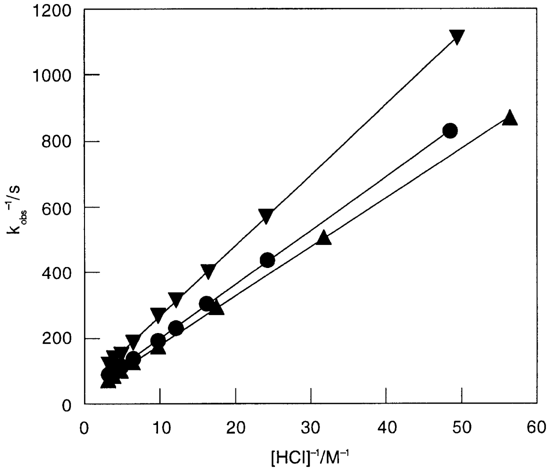


Fig. 5. Double reciprocal plot for observed rate constants for hydrolytic decomposition of PB in water (▲), 20:80 (v/v) dioxane/water (●) and 30:70 (v/v) dioxane/water (▼) solutions.

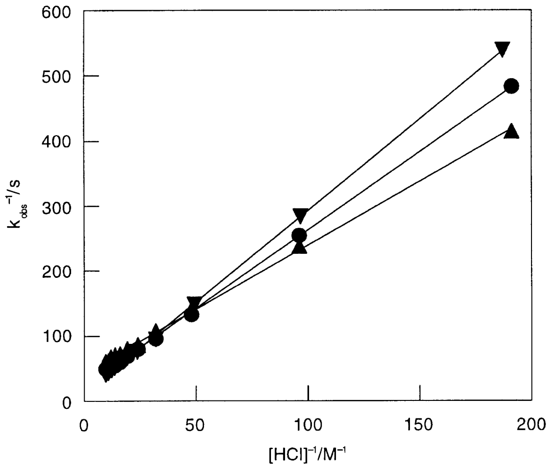


Fig. 6. Double reciprocal plot for observed rate constants for hydrolytic decomposition of IP in water (▲), 20:80 (v/v) dioxane/water (●) and 30:70 (v/v) dioxane/water (▼) solutions.

than that of PB and IP, in agreement with the stronger acidity of naphthyl vs. phenyl derivatives commonly observed [10].

Comparison of the values given in Table 1 also shows clear solvent effects. Interestingly, in the case of PB a decrease in solvent polarity leads to a decrease in the reactivity and acidity of the imine moiety, whereas in the case of IP the opposite trend is observed. These results can be interpreted based on the opposite changes in dipole moment associated with these two substrates. In the case of PB, the cationic form **I** [Scheme 1, Ar = $C_6H_4NH(CH_3)_2^+$] is predicted to be *more* polar than the corresponding dication **II**. Thus, as the solvent polarity decreases, K_a is expected to decrease as well. Furthermore, nucleophilic attack of water molecules leading to the formation of a tetrahedral carbinolamine intermediate would result in an *increase* in dipole moment and, consequently, the rate of the reaction is expected to decrease as the polarity of the solvent also decreases. On the other hand, in the case of IP the neutral form I (Scheme 1, Ar = C_6H_4OH) is predicted to be *less* polar than the corresponding cation II. Thus, as the solvent polarity decreases, Ka increases. Moreover, nucleophilic attack of water molecules would lead to a *decrease* in dipole moment and thus the rate of the reaction is expected to increase as the polarity of the solvent decreases. It should be pointed out here that the relative changes in dipole moment predicted for the conjugate pairs I/II for PB and IP are indeed consistent with results obtained from MOPAC/AM1 calculations. Finally, one could assume that the trends observed for PB $k_{\text{hydrolysis}}$ and K_a values with solvent polarity would correspond to IPB as well. In fact, the observed rate constants for IPB decrease with decreasing solvent polarity as in the case of PB. However, since no K_a value could be determined for IPB, the solvent dependence of the kinetic parameter $k_{\text{hydrolysis}}/K_a$ for this substrate could not be analyzed any further.

In summary, the dependence on pH of the observed rate constants for hydrolysis of PB, IP and IPB in HCl solutions is consistent with rate-determining carbinolamine formation by nucleophilic attack of water on the protonated imine moiety. The effects on changing the solvent from water to 30% dioxane on the pKa and reactivity of the iminium ions depend strongly on the nature of the Ar group on the nitrogen. While a decrease in the rate of hydrolysis is observed with decreasing solvent polarity when Ar has a polar electron-withdrawing group, the opposite results in the presence of a neutral electron-donating substituent. Consequently, acid catalysed hydrolysis of quinone-imine dyes may remain efficient even in solvents of low ionizing power.

3. Experimental

Indophenol blue (Aldrich) was purified by column chromatography on silica gel using ethyl acetate:petroleum ether (3:1) as eluent. Indophenol (sodium salt) and phenol blue (both from Aldrich) were used as received; their identity was checked by means of ^1H NMR spectroscopy using a Bruker Model AM-250 NMR spectrometer. 1,4-Dioxane (BDH, ACS grade) was fractionally distilled before use. Aqueous solutions were prepared using analytical grade chemicals (BDH) and water purified by passage through a Millipore apparatus.

The hydrolysis of quinone-imine dyes in HCl aqueous solutions was monitored spectrophoto metrically using a Varian Cary 1 Bio spectrophoto mether with a thermostated cell compartment connected to a heated/refrigerated circulating bath (VWR Scientific Model 1160A). Reactions were initiated by adding the substrate (dissolved in water or in dioxane) to a solution containing all the other constituents, with the exception of the series of reactions for hydrolysis of PB in water, which were initiated by adding the required aliquot of HCl (from a ca. 1 N stock aqueous solution) to a solution containing all the other constituents. Typical substrate concentrations were in the order of 5×10^{-5} M, 1×10^{-4} M and 3×10^{-4} M for PB, IP and IPB, respectively. 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 0.5 M using NaCl as compensating electrolyte. All measurements were carried out at (25.0 ± 0.1)°C. Kinetic traces were determined by monitoring the disappearance of the quinone-imine dye at the corresponding wavelength of maximum absorption in the visible region (i.e. λ_{max} ca. 570, 495 and 430 nm for PB, IP and IPB, respectively). Values of the observed rate constants were then obtained by fitting the kinetic traces to a single exponential function by using the general curve fitting procedure of Kaleidagraph software (version 3.0.5) from Abelbeck Software. Molecular modeling calculations were carried out using the MOPAC/AM1 method of Chem3D (CambridgeSoft Corporation version 4.0).

Acknowledgements

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

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