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KINETICS AND MECHANISM OF THE DIAZO COUPLING REACTION OF ARYLDIAZO PHENYL SULPHIDES WITH β-NAPHTHOL IN ACID SOLUTIONS

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ABSTRACT. The diazo coupling reaction of aryldiazo phenyl sulphides with β-naphthol in solutions of dioxane and ethanol acidified with hydrochloric acid was studied. The kinetics of formation of azo dyes were investigated at 25°C under pseudo-first-order conditions. Over the range of HCl concentrations studied, pseudo-first-order rate constants were obtained and the reaction was found to be of first order in diazo sulphide. The observed rate constants (k_{obs}) were found to be independent of acid concentration, and the reaction was only affected by the basicity of the diazo sulphide and the nature of the solvent. Two possibilities for the mechanism of azo dye formation have been deduced and one possible mechanism for this characteristic reaction is supported by the present investigation.

INTRODUCTION

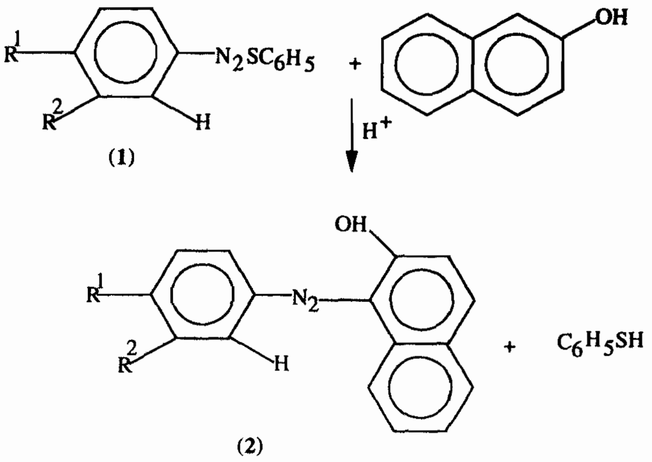
In connection with our studies of diazo derivatives in which the diazo group is involved but remains functionally intact [1-4], it was found necessary to study the diazo coupling reaction of aryldiazo phenyl sulphides, ArN_2Sph, with β-naphthol under various conditions.

The previous paper [1] was concerned with the preparation of aryldiazo phenyl sulphides. The coupling ability of these compounds was explored. The products of the reaction of a series of aryldiazo phenyl sulphides with β-naphthol in aqueous ethanol have also been reported [1].

In the earlier paper [1], an attempt was made to study the kinetics of formation of para red (**3c**) [1] from the reaction of *p*-nitrobenzenediazo phenyl sulphide (**2c**) [1] with β-naphthol in acetone solution acidified with acetic acid. It has been shown later [2] that diazo components react with acetone in acid media to give the corresponding α-oxopropanal arylhydrazone in high yield [2]. Since the technique used earlier [1] in following the rate of formation of para red was unsuitable, the results obtained were never conclusive and it was not possible to elucidate the mechanism of the coupling activity of the substrate (**2c**) [1] which was investigated as a representative of aryldiazo phenyl sulphides.

The present paper reports a study of the diazo coupling reaction of aryldiazo phenyl sulphides (**1a– i**) with β-naphthol under various conditions in an attempt to clarify the mechanism of the decomposition of aryldiazo phenyl sulphides (**1**) which exemplifies production of diazonium ions by suitable treatment [3 – 6]. Dioxane and ethanol were chosen as solvents, after it had been ascertained that no other products were formed in hydrochloric acid solutions. It was established that the reactions were clean in all cases examined, and the reaction products were always the corresponding azo dyes (**2**).

	R^1	R^2
a	OCH_3	H
b	OC_2H_5	H
c	CH_3	H
d	H	H
e	Cl	H
f	Br	H
g	CO_2H	H
h	H	NO_2
i	NO_2	H



The diazo coupling reaction of the substrates (**1**) with β-naphthol in dioxane, and ethanol was studied by spectrophotometric monitoring the appearance of absorption of the corresponding dye (**2**) at its visible absorbance maximum. No reaction was observed in dry organic solvents. The production of colour was accelerated by acids. Accordingly, the effect of hydrochloric acid in dioxane and ethanol solutions, on the reaction rate was examined at 25°. Reactions were carried out under pseudo-first-order conditions (β-naphthol was required in large excess, and its concentration (4.5×10^{-3}M) remained constant, and at least a 1090-fold excess of HCl over the diazo sulphides examined were used throughout). The wavelength for the kinetic runs corresponded to λ_{max} for the dye. Thus the reaction proceeded with an increase in absorption and was assumed to be proportional to the concentration of the diazo sulphide (c_{DS}) reacted. In all cases, the extent of the reaction exceeds 98%.

RESULTS AND DISCUSSION

The observed rate constants for the diazo coupling reaction of diazo sulphides (**1a-i**) with β-naphthol under a variety of conditions are given in Table 1. In all cases excellent adherence to a first-order behaviour over five half-lives was observed throughout the kinetic runs. Typical first-order plots are shown in Figure 1. In addition to displaying first-order kinetics, the measured rate constants (k_{obs}) were appropriately independent of hydrochloric acid concentrations over the range used (from 0.06 to 1.0 M). Kinetic studies were carried out at five different concentrations of hydrochloric acid with all the diazo sulphides examined (**1a-i**), the initial diazo sulphide concentrations being *ca.* 10^{-5} M throughout (see Table 1). The first-order rate constants (k_{obs}) remained constant within experimental accuracy.

The data listed in Table 1 show that the values of k_{obs} are markedly affected by the nature of the solvent. Thus the increase in k_{obs} in passing from dioxane to ethanol is evident.For each compound, the observed rate constant in ethanol is 6 times higher than the corresponding value in dioxane.

Measurements were made on nine substrates, these encompassed, nine orders of magnitude in reactivity and ranged from p-methoxybenzenediazo (**1a**), most reactive to *p*-nitrobenzenediazo (**1i**),

Table 1. Rate constants for HCl-catalyzed diazo coupling reaction of aryldiazo phenyl sulphides (**1a – i**) with β-naphthol in dioxane, and ethanol at 25°[a].

Compound	[HCl] / M	$10^5 k_{obs}$ / s^{-1} (Dioxane)	$10^5 k_{obs}$ / s^{-1}(Ethanol)
(1a)[b]	0.06	52.21	316.3
	0.10	52.24	319.9
	0.40	51.75	316.3
	0.80	52.72	314.4
	1.00	52.21	318.1
	Average	52.23 ± 0.49	317.2 ± 2.8
(1b)[c]	0.06	47.68	291.2
	0.10	47.91	291.2
	0.40	47.45	287.5
	0.80	47.68	289.4
	1.00	47.45	287.5
	Average	47.68 ± 0.23	289.3 ± 1.9
(1c)[b]	0.06	37.86	228.4
	0.10	38.14	227.7
	0.40	37.86	229.0
	0.80	38.41	230.7
	1.00	38.41	230.0
	Average	38.13 ± 0.28	229.2 ± 1.5
(1d)[c]	0.06	22.72	135.6
	0.10	22.33	136.1
	0.40	22.42	135.6
	0.80	22.61	135.1
	1.00	22.54	135.1
	Average	22.52 ± 0.20	135.6 ± 0.50
(1e)[c]	0.06	10.95	65.10
	0.10	10.86	66.31
	0.40	11.04	65.55
	0.80	10.86	66.70
	1.00	11.04	66.13
	Average	10.95 ± 0.09	65.96 ± 0.86
(1f)[d]	0.06	10.74	64.79
	0.10	10.83	64.79
	0.40	10.67	65.32
	0.80	10.79	64.40
	1.00	10.74	65.10
	Average	10.76 ± 0.09	64.9 ± 0.50
(1g)[d]	0.06	9.61	57.50
	0.10	9.55	58.19
	0.40	9.61	57.98
	0.80	9.63	58.08
	1.00	9.59	57.50
	Average	9.60 ± 0.05	57.94 ± 0.44

Table 1 Continued.

(1h)^{c}	0.06	2.37	14.38
	0.10	2.39	14.38
	0.40	2.42	14.49
	0.80	2.39	14.56
	1.00	2.42	14.56
	Average	2.39 ± 0.03	14.48 ± 0.10
(1i)^{d}	0.06	1.96	11.80
	0.10	1.93	11.68
	0.40	1.93	11.80
	0.80	1.95	11.68
	1.00	1.96	11.73
	Average	1.94 ± 0.02	11.73 ± 0.07

[a] Concentration varies from 4.5 x 10^{-5} M (for (**1i**)) to 5.5 x 10^{-5} M (for (**1a**)), [β-naphthol] = 4.5 x 10^{-3} M. [b] λ_{max} 470 nm. [c] λ_{max} 480 nm. [d] λ_{max} 490 nm.

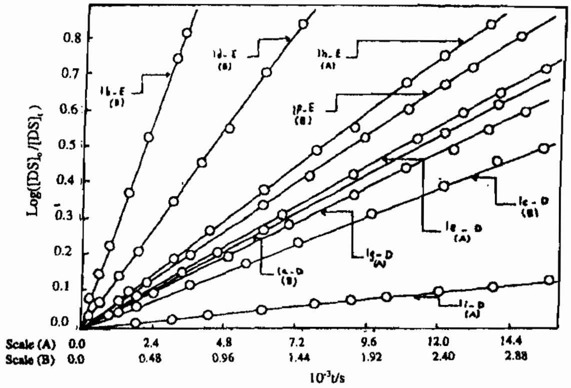


Figure 1. Representative of pseudo-first-order kinetic plots for the diazo coupling reaction of aryldiazo phenyl sulphides with β-naphthol in dioxane [D] and ethanol [E] at 25°. Reactions were carried out at initial concentrations of diazo sulphides *ca.* 10^{-5} M throughout (Table 1), β-naphthol 4.5 x 10^{-3} M and [HCl], 1M.

least reactive] phenyl sulphide. The other seven in order of decreasing reactivity, were **1b** > **1c** > **1d** > **1e** > **1f** > **1g** > **1h**. Figure 2 demonstrates that the activities of the diazo sulphides (**1a-i**) could be correlated with the Hammett substituent constant (σ_x). The value for such correlation was negative, indicating that electron-withdrawing substituents decrease the basicity of (**1**) [5].

Mechanism of reaction. The fact that the observed reaction rates are independent of the concentration of hydrochloric acid, as well as the effect of electron-withdrawing substituents in the benzenediazo residue of substrates resulting in decreased k_{obs} values, are consistent with the following scheme (Equations 1 – 3):

$$\mathrm{DS} + \mathrm{H}^{+} \rightleftharpoons \mathrm{DSH}^{+}\ \text{(fast, pre-equilibrium)} \qquad (1)$$

$$\mathrm{DSH}^{+} \xrightarrow{k} \mathrm{D}^{+} + \mathrm{C_6H_5SH} \qquad (2)$$

$$\mathrm{D}^{+} + \mathrm{HOC_{10}H_7}\text{-}\beta \longrightarrow \mathrm{ArN_2C_{10}H_6(OH)}\text{-}\beta + \mathrm{H}^{+} \qquad (3)$$

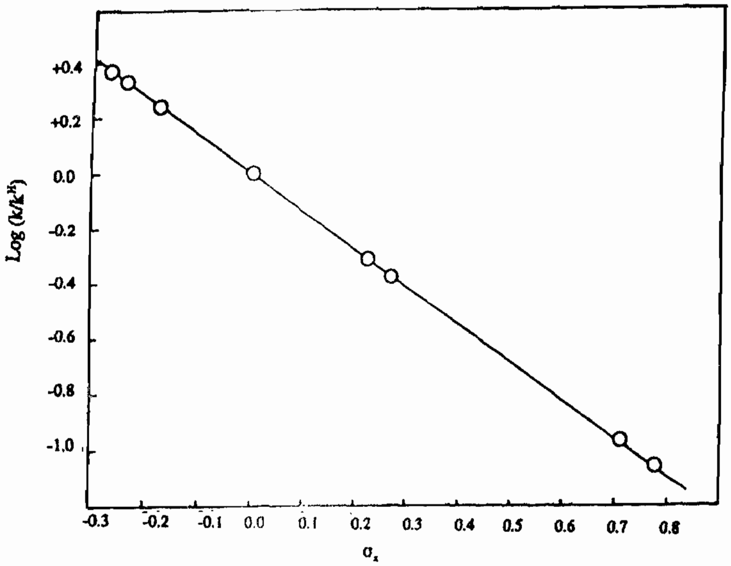


Figure 2. Plot of log k/k^H for the HCl catalyzed decomposition of *m*- and *p*-substituted beenzenediazo phenyl sulphides versus Hammett σ_x values of the substituent. Slope is -1.40.

If the slow step is the unimolecular decomposition of the protonated substrate DSH$^+$ to give the diazonium ion, D$^+$ (Equation 2), which instantly reacts with β-naphthol to give products, the rate of loss of the sum of the equilibrium concentrations of DS and DSH$^+$ can be represented by Equation (4) where k is the rate constant for the slow step (Equation 2) and f^* is the activity coefficient of the transition state for that step.

$$\frac{-d(C_{DS}{}^{+}\ C_{DSH}{}^{+})}{dt} = KC_{DSH}{}^{+}\left(\frac{f_{DSH}{}^{+}}{f^{*}}\right) \qquad (4)$$

The experimental first-order rate constant (k_{obs}) is defined by Equation 5. Combination of equations 4 and 5, together with the expression for the acid ionization constant $K_{DSH}{}^{+}$ of DSH^{+}, gives Equation 6. The hydrogen ion activity ($a_{H}{}^{+}$) can be expressed in terms of the Hammett acidity function according to Equation 7 in which B represents any neutral base. Substitution in Equation 6 for $a_{H}{}^{+} = h_{o} f_{BH}{}^{+} / f_{B}$ [4], leads to Equation 8.

$$k_{obs} = -\left(\frac{1}{C_{DS} + C_{DSH^{+}}}\right) \frac{d(C_{DS} + C_{DSH^{+}}}{dt} \qquad (5)$$

$$k_{obs} = \left(\frac{C_{DS}}{C_{DS} + C_{DSH^{+}}}\right) \frac{k}{K_{DSH^{+}}} \frac{a_{H^{+}} f_{DS}}{f^{*}} \qquad (6)$$

$$H_{o} = -\log h_{o} = -\log \left(\frac{a_{H^{+}} f_{B}}{f_{BH^{*}}}\right) \qquad (7)$$

$$k_{obs} = \left(\frac{C_{DS}}{C_{DS} + C_{DSH^{+}}}\right) \frac{k}{K_{DSH^{+}}} h_{o} \frac{f_{DS} f_{BH^{+}}}{f_{B} f^{*}} \qquad (8)$$

Under the conditions of the diazo coupling reaction of the diazo sulphides with β-naphthol being considered [3, 4], two situations arise depending upon the relative values of h_{o} and $K_{DSH}{}^{+}$.

Firstly if $h_{o} < K_{DSH}{}^{+}$, then only minor quantities of DSH^{+} exist in the pre-equilibrium mixture. $c_{DSH}{}^{+}$ can be neglected with respect to c_{DS} and Equations 6 and 8 reduce to Equations 9 and 10.

$$k_{obs} = \frac{k}{K_{DSH^{+}}} \frac{a_{H^{+}} f_{DS}}{f^{*}} \qquad (9)$$

$$k_{obs} = \frac{k}{K_{DSH^{+}}} h_{o} \frac{f_{DS} f_{BH^{+}}}{f_{B} f^{*}} \qquad (10)$$

It follows from Equation 9 that k_{obs} is proportional to h_0, or to the activity of hydrogen ion. The lack of correlation between k_{obs} and a_H^+ over the range of the hydrochloric acid concentrations studied [3] implies that the first possibility is not applicable to this experimentally recognizable case.

Alternatively when $h_0 > K_{DSH}{}^+$ whereas $H_0 < pK_{DSH}{}^+$, all the substrate, DS, is rapidly and stoicheiometrically converted into the protonated substrate, DSH^+, in the pre-equilibrium step (Equation 1). $c_{DSH}{}^+ >> c_{DS}{}^+$ and Equations 6 and 8 therefore reduce to

$$k_{obs} = \frac{f_{DSH}{}^+}{f^*} \qquad (11)$$

Thus if $f_{DSH}{}^+/f^*$ is constant for all acid concentrations then the observed reaction rate will be independent of HCl concentration and will stay approximately constant. Accordingly, the reaction under investigation obeys Equation 11. It can therefore be concluded that the diazo coupling reaction of aryldiazo phenyl sulphides with β-naphthol proceeds in accord with the above mechanism, and is in agreement with the results.

EXPERIMENTAL

Materials. All the diazo sulphides used in this investigation have been prepared by the method described earlier [1]. The b.p. of the compounds recorded in Table 2 have not been described previously [1], and all are pale yellow oils. *p*-Phenetidine (4-ethoxyaniline) was prepared by reduction of p-nitrophenetole (Aldrich) with iron and hydrochloric acid. A mixture of *p*-nitrophenetole (50 g, 50 g, 0.3 mole) and iron borings (50 g) was added slowly to ice water (100 mL), followed by hydrochloric acid (10 mL; sp. gr. 1.16). A vigorous reaction was started by the addition of a few drops of 10% platinum chloride solution. When the reduction was finished (8 h), the mixture made just alkaline with 10 % sodium hydroxide solution, the base was set free as an oil, and the liquid was allowed to settle for 3 h. The aqueous layer run off, and the remaining mass mixed with sawdust and extracted three times with toluene. *p*-Phenetidine was obtained by fractional distillation of the extract as a colourless oil, b.p. 254° [7] (yield 32.8 g; 80 %).

This alternative procedure proved to be much applicable than that reported in the literature [8]. It is claimed that the reduction of *p*-nitrophenetole is affected by tin and hydrochloric acid [8, 9].

β-Naphthol was available from previous work [1, 3- 5] and the references in [1] and [5]. Dioxane, and ethanol were purified by standard methods and dried as described earlier [3, 5]. Acid solutions (hydrochloric acid was used) were prepared and dried using the technique described before [3, 4]. HCl concentrations were determined by titration with sodium borate [3].

Diazo coupling of aryldiazo phenyl sulphides. Diazo coupling of *p*-methoxyphenyl-, *p*-tolyl-, phenyl-, *p*-chlorophenyl-, *p*-bromophenyl-, *p*-carboxyphenyl-, *m*-nitrophenyl-, and *p*-nitrophenyl diazo phenyl sulphide with β-naphthol in hydrochloric acid solutions of dioxane and of ethanol gave the corresponding azo dyes in quantitative yield. In colours and m.p. these dyes agreed with descriptions given before in [1, 5], and references therein.

Table 2. Aryldiazo phenyl sulphides prepared from diazonium chlorides and thiophenol following the procedure described in a previous paper [1].

Ar in $ArN_2SC_6H_5$ (**1**)	B.p. / mm Hg	Formula (MW)	Analytical results (%)				
				C	H	N	S
p-$OCH_3C_6H_4$ (**1a**)	185-186/22	$C_{13}H_{12}N_2OS$ (244.33)	Calcd. Found	63.90 63.87	4.96 5.01	11.47 11.50	13.12 13.09
p-$OC_2H_5C_6H_4$ (**1b**)	205/50	$C_{14}H_{14}N_2OS$ (258.36)	Calcd. Found	65.08 65.10	5.47 5.45	10.84 10.82	12.41 12.42
p-MeC_6H_4 (**1c**)	178/16	$C_{13}H_{12}N_2S$ (228.33)	Calcd. Found	68.38 68.35	5.31 5.30	12.27 12.31	14.04 14.04
C_6H_5 (**1d**)	149-150/19	$C_{12}H_{10}N_2S$ (214.30)	Calcd. Found	67.25 67.20	4.71 4.73	13.08 13.10	14.96 14.95

*p-Ethoxybenzeneazo-2-naphthol (**2b**).* Diazo coupling of *p*-ethoxyphenyl diazo phenyl sulphide (2 m) with β-naphthol (0.5 g, 3 m) in hydrochloric acid solutions of dioxane and of ethanol (10 mL) resulted in the isolation of brilliant red needles (0.56 g; 96 %), m.p. 148–149°. Found C, 74.01; H, 5.52; N, 9.58, Cald. for $C_{18}H_{16}N_2O_2$ (292.36) : C, 73.94; H, 5.53; N, 9.58 %.

Kinetic measurements. Rates of reaction were determined by spectrophotometric analysis for azo dyes using a Bausch and Lomb spectronic 21 UVD spetrophotometer. Adequate accounts have been given previously [3 – 6]. Reactions were studied under pseudo-first-order conditions, with β-naphthol and hydrochloric acid in excess [3]. Time measurements were made with a calibrated stop watch. The measured first-order rate constants (k_{obs}) were obtained from plots of log $([DS]_0 / [DS]_t)$ versus time. Thus, $k_{obs} = (2.3 / t) \log ([DS]_0 / [DS]_t)$ where subscripts o and t refer to zero time and time t, respectively.

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