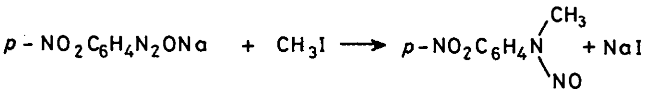
Kinetics and Mechanism of the Diazo Coupling Reaction of Arenediazo Methyl Ethers with β-Naphthol. Part 1. The Rates of Reaction in Nonaqueous Acid Solutions

Nabil K. Masoud* and Mona F. Ishak
Chemical Department, Ministry of Industry, 12 Ramses Street, Cairo, Egypt

Rate data are presented for the diazo coupling reaction of arenediazo methyl ethers with β-naphthol in solutions of dioxane, ethanol, and propan-2-ol acidified with hydrochloric acid at 25 °C. 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 ether. The relationship between the observed rate constants ($k_{obs.}$) and hydrochloric acid concentration (c_{HCl}) was found to be non-linear. Correlations of reaction rates with the Hammett acidity function (H_0) and with the Hammett substituent constant (σ_x) conform with a mechanism in which the slow step is unimolecular decomposition of the protonated diazo ether, DEH$^+$, to the coupling entity, the diazonium ion, D$^+$, which instantly reacts with β-naphthol to give the azo dye.

Arenediazo methyl ethers are generally produced by the action of methyl halides on metallic diazoates. They are interesting compounds from both a structural and a chemical point of view. Structurally, since there are two isomers of diazoates, the normal and the iso, two corresponding series of ethers were expected, but such was not the case. Pechmann and Frobenius[1] showed that the nature of the product is not determined by the series to which the salt belongs, but by the metal used. Thus, sodium *p*-nitrobenzeneisodiazoate affords *N*-nitroso-*p*-nitromethylaniline (I), whereas the silver salt leads to the corresponding arenediazo methyl ether (II), when both were treated with methyl iodide. Moreover, silver benzenediazoate and silver benzeneisodiazoate when treated with methyl iodide give the same compound (benzenediazo methyl ether).[2]



$$p\text{-}NO_2C_6H_4N_2ONa + CH_3I \longrightarrow p\text{-}NO_2C_6H_4N(CH_3)NO + NaI$$

(I)

m.p. 100 °C

$$p\text{-}NO_2C_6H_4N_2OAg + CH_3I \longrightarrow p\text{-}NO_2C_6H_4N_2OCH_3 + AgI$$

(II)

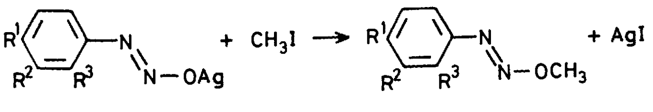
m.p. 83 °C

There has been much controversy as to whether the arenediazo methyl ethers are to be considered as normal or iso compounds, and although much work has been done on this point,[3–6] it remains undetermined.

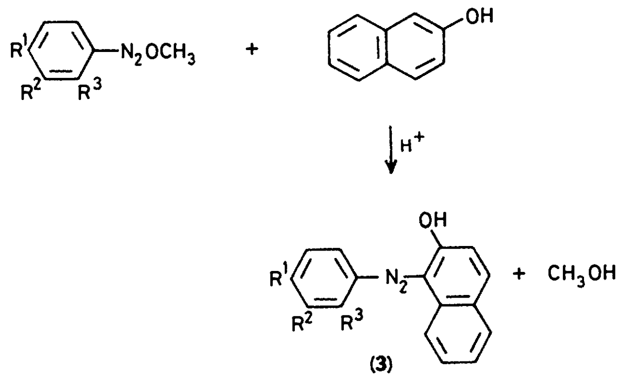
Little appears to be known about the chemistry of these compounds, but it has been reported that compound (II) couples with β-naphthol both in aqueous and in benzene solution.[7] So far, no systematic study has been carried out on the mechanism of the decomposition of arenediazo methyl ethers which exemplifies production of diazonium ions by suitable treatment.[8,9]

This paper reports a study of the diazo coupling reaction of arenediazo methyl ethers with β-naphthol under various conditions in an attempt to elucidate the mechanism of their coupling activity.

The benzene and substituted benzenediazo methyl ethers utilised in this investigation were prepared from the corresponding silver benzeneisodiazoate (**1a**—**f**) and methyl iodide (see Experimental section), according to the method of Pechmann and Frobenius.[1] Coupling of compounds (**2a**—**f**) with β-naphthol in acid media (hydrochloric acid was used), in the presence of an appropriate organic solvent, resulted in almost quantitative yields of the azo dyes (**3a**—**f**).



(**1**) (**2**)



(**3**)

a; R¹ = R² = R³ = H
b; R¹ = Br, R² = R³ = H
c; R¹ = Cl, R² = R³ = H
d; R¹ = CN, R² = R³ = H
e; R¹ = R³ = H, R² = NO₂
f; R¹ = NO₂, R² = R³ = H

An organic solvent was sought which (i) is miscible with water and with the compounds under investigation, (ii) is unaffected by acids, and (iii) does not interact with the reactants or any intermediate, in the presence of acids. Dioxane, ethanol, and propan-2-ol were proposed, after it had been ascertained that no other products were formed in hydrochloric acid solutions. Other solvents, such as acetone, were excluded because they did not meet conditions (ii) and (iii).

The diazo coupling reaction of the substrates (**2**) with β-naphthol in dioxane, ethanol, and propan-2-ol was studied by spectrophotometric observation of the corresponding dye (**3**) at a wavelength close to its visible absorbance maximum. No

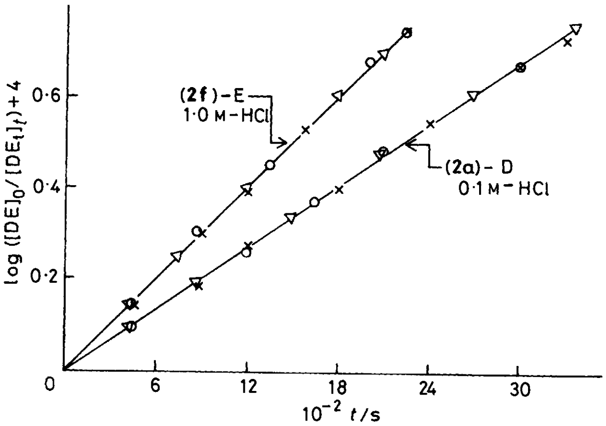


Figure 1. Effect of change of β-naphthol concentration on the overall rate of decomposition of the arenediazo methyl ethers at 25 °C: 10^4[β-naphthol] ×, 5.5; ○, 45; ▽, 720. D = Dioxane, E = ethanol

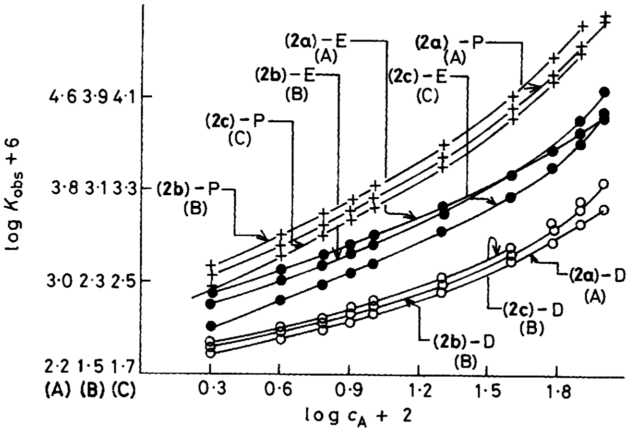


Figure 2. Variation of reaction rates with [HCl] for the decomposition of compounds (**2a**—**c**) in dioxane (D), ethanol (E), and propan-2-ol (P) at 25 °C

reaction was observed in dry organic solvents. The reaction was accelerated by acids. Accordingly, the effect of hydrochloric acid was examined at 25 °C. Reactions were carried out under pseudo-first-order conditions (a 100-fold excess of β-naphthol and at least a 400-fold excess of HCl over the diazo ethers examined were used throughout). Under these conditions, it was observed that the reaction showed no marked variation in the rate of decomposition of the arenediazo methyl ethers with varying concentrations of β-naphthol (Figure 1). Previous to the kinetic investigation, the reaction between each compound (**2**) and β-naphthol in the three different solvents at HCl concentrations of 0.02 and 1M was carried out to isolate the products. In every case, the product was the corresponding dye (**3**). The wavelength for the kinetic runs corresponded to that at which the greatest difference in absorbance between the reactants and the products occurred. In each case, this wavelength was found to be at $\lambda_{max.}$ for the dye and was located at 470 nm. Thus the reaction proceeded with an increase in absorption and was assumed to be proportional to the concentration of the diazo ether (c_{DE}) reacted. It is to be noted that, in all cases examined, the extent of the reaction exceeds 98%.

Results and Discussion

Reaction Rates.—Each system showed good first-order behaviour over three half-lives. Typical first-order plots are shown in Figure 1. Values of $k_{obs.}$ obtained under a variety of conditions are in the Table.

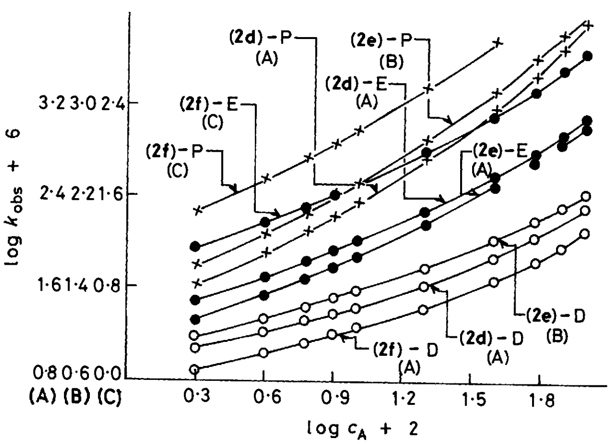


Figure 3. Variation of reaction rates with [HCl] for the decomposition of compounds (**2d**—**f**) in dioxane (D), ethanol (E), and propan-2-ol (P) at 25 °C

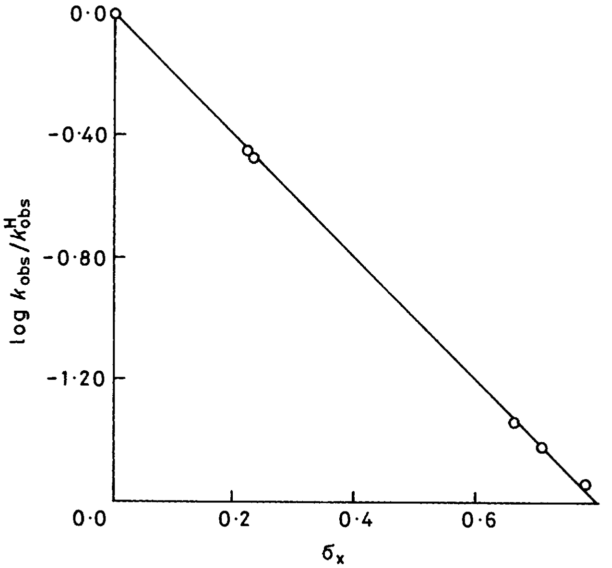


Figure 4. Plot of log k_{obs}/k^{H}_{obs} for the HCl-catalysed decomposition of *m*- and *p*-substituted benzenediazo methyl ethers *versus* Hammett σ_x values of the substituents. [HCl] 1M. Slope ρ is −2.03

Figures 2 and 3 obtained from the data in the Table represent the logarithmic plots of $k_{obs.}$ *versus* c_A. In spite of the fact that the reaction under investigation was catalysed by acid, a non-linear relationship was manifested. This result may indicate that the reaction is influenced by the acidity of the medium.[10]

The correlation between the rate constants (k_{obs}) and the H_0 acidity function[11–14] for the HCl-catalysed decomposition of benzenediazo methyl ether and its substituted derivatives in dioxane and ethanol is reported in the Table. For each compound, an approximately constant value of (log k_{obs} + H_0) is evident in both organic solvents.

The relevant values of the acidity function (H_0) for solutions of hydrochloric acid in propan-2-ol and propan-2-ol–water mixtures are not at present available,[15] and will be the subject of further investigation.

In addition, the Table shows that for each compound examined, the relative magnitudes of k_{obs} in the different solvents at one acid concentration are somewhat dependent upon each other, but mostly increase in the order dioxane

Rate constants for HCl-catalysed diazo coupling reaction of unsubstituted and substituted benzenediazo methyl ethers (**2**) with β-naphthol in dioxane, ethanol, and propan-2-ol at 25 °C.[a] The acidity function H_0 of the medium in dioxane and ethanol is also given

		Dioxane			Ethanol			Propan-2-ol
Compound	[HCl]/M	$10^4k^d_{obs}/s^{-1}$	H_0^e	$\log k_{obs} + 6 + H_0$	$10^3k^d_{obs}/s^{-1}$	H_0^e	$\log k_{obs} + 6 + H_0$	$10^2k^d_{obs}/s^{-1}$
(**2a**)[b]	0.02	2.40	+1.65	4.03	0.83	+1.36	4.28	0.12
	0.04	3.16	+1.59	4.09	1.32	+1.04	4.16	0.22
	0.06	3.80	+1.54	4.12	1.74	+0.87	4.11	0.33
	0.08	4.57	+1.45	4.11	2.19	+0.73	4.07	0.44
	0.10	5.25	+1.35	4.07	2.69	+0.61	4.05	0.59
	0.20	8.32	+1.15	4.07	4.79	+0.30	3.98	1.26
	0.40	15.14	+1.03	4.21	9.12	+0.12	4.08	3.31
	0.60	22.91	+0.94	4.30	14.13	+0.02	4.17	6.31
	0.80	33.11	+0.81	4.33	20.89	−0.30	4.02	11.48
	1.00	45.71	+0.40	4.06	28.18	−0.39	4.06	19.05
(**2b**)[c]	0.02	0.52	+1.65	3.37	0.13	+1.36	3.46	0.03
	0.04	0.76	+1.59	3.47	0.21	+1.04	3.36	0.05
	0.06	0.91	+1.54	3.50	0.29	+0.87	3.33	0.08
	0.08	1.10	+1.45	3.49	0.36	+0.73	3.29	0.10
	0.10	1.26	+1.35	3.45	0.44	+0.61	3.25	0.14
	0.20	2.00	+1.15	3.45	0.79	+0.30	3.20	0.32
	0.40	3.63	+1.03	3.59	1.66	+0.12	3.34	0.83
	0.60	5.50	+0.94	3.68	2.88	+0.02	3.48	1.82
	0.80	8.92	+0.81	3.76	5.25	−0.30	3.42	3.47
	1.00	15.49	+0.40	3.59	9.55	−0.39	3.59	6.46
(**2c**)[b]	0.02	0.58	+1.65	3.41	0.13	+1.36	3.48	0.03
	0.04	0.83	+1.59	3.51	0.22	+1.04	3.38	0.06
	0.06	1.00	+1.54	3.54	0.30	+0.87	3.35	0.08
	0.08	1.20	+1.45	3.53	0.38	+0.73	3.31	0.12
	0.10	1.38	+1.35	3.49	0.48	+0.61	3.29	0.15
	0.20	2.23	+1.15	3.50	0.91	+0.30	3.26	0.34
	0.40	4.07	+1.03	3.64	1.82	+0.12	3.38	0.91
	0.60	6.62	+0.94	3.76	3.31	+0.02	3.54	1.78
	0.80	10.50	+0.81	3.83	5.02	−0.30	3.40	3.16
	1.00	16.22	+0.40	3.61	9.77	−0.39	3.60	6.76
(**2d**)[b]	0.02	0.12	+1.65	2.72	0.03	+1.36	2.86	0.004
	0.04	0.17	+1.59	2.81	0.05	+1.04	2.76	0.008
	0.06	0.21	+1.54	2.86	0.07	+0.87	2.71	0.013
	0.08	0.24	+1.45	2.83	0.09	+0.73	2.67	0.017
	0.10	0.28	+1.35	2.79	0.11	+0.61	2.65	0.023
	0.20	0.44	+1.15	2.79	0.20	+0.30	2.59	0.055
	0.40	0.76	+1.03	2.91	0.40	+0.12	2.72	0.151
	0.60	1.15	+0.94	3.00	0.62	+0.02	2.81	0.288
	0.80	1.59	+0.81	3.01	0.91	−0.30	2.66	0.525
	1.00	2.08	+0.40	2.72	1.29	−0.39	2.72	0.871
(**2e**)[c]	0.02	0.10	+1.65	2.73	0.02	+1.36	2.68	0.004
	0.04	0.14	+1.59	2.73	0.04	+1.04	2.58	0.008
	0.06	0.17	+1.54	2.78	0.05	+0.87	2.55	0.011
	0.08	0.21	+1.45	2.77	0.06	+0.73	2.52	0.016
	0.10	0.24	+1.35	2.73	0.08	+0.61	2.49	0.021
	0.20	0.39	+1.15	2.74	0.15	+0.30	2.46	0.051
	0.40	0.69	+1.03	2.87	0.32	+0.12	2.62	0.138
	0.60	1.02	+0.94	2.95	0.53	+0.02	2.74	0.263
	0.80	1.32	+0.81	2.93	0.76	−0.30	2.58	0.437
	1.00	1.74	+0.40	2.64	1.07	−0.39	2.64	0.724
(**2f**)[c]	0.02	0.08	+1.65	2.53	0.01	+1.36	2.52	0.003
	0.04	0.11	+1.59	2.63	0.02	+1.04	2.42	0.006
	0.06	0.13	+1.54	2.66	0.03	+0.87	2.39	0.009
	0.08	0.16	+1.45	2.65	0.04	+0.73	2.35	0.012
	0.10	0.18	+1.35	2.61	0.05	+0.61	2.33	0.016
	0.20	0.28	+1.15	2.59	0.10	+0.30	2.30	0.035
	0.40	0.48	+1.03	2.71	0.21	+0.12	2.44	0.096
	0.60	0.72	+0.94	2.80	0.35	+0.02	2.56	0.191
	0.80	0.96	+0.81	2.79	0.53	−0.30	2.42	0.316
	1.00	1.32	+0.40	2.52	0.76	−0.39	2.49	0.526

[a] Concentration varies from 3.5×10^{-5}M [for (**2f**)] to 5.5×10^{-5}M [for (**2a**)]. [b] $\lambda_{max.}$ 480 nm. [c] $\lambda_{max.}$ 490 nm. [d] Average of at least two runs, rates were reproducible to ±4%. [e] H_0 values taken from ref. 11.

< ethanol < propan-2-ol. The data encompassed six orders of magnitude in reactivity and ranged from *p*-nitrobenzenediazo [(**2f**), least reactive] to benzenediazo [(**2a**), most reactive] methyl ether. The other four in order of decreasing reactivity were *p*-chlorobenzenediazo (**2c**) > *p*-bromobenzenediazo (**2b**) > *p*-cyanobenzenediazo (**2d**) > *m*-nitrobenzenediazo (**2e**) methyl ether. Figure 4 indicates that the activities of the compounds (**2a—f**) at a constant HCl concentration of 1M 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 (**2**).

The kinetic data reveal the fact that the proton-transfer reaction ($DE + H^+ \rightleftharpoons DEH^+$) precedes the rate-determining step. This would be expected to be most difficult in cases where the general electron density is lowest, *i.e.* with the *p*-nitro compound (**2f**).

Mechanism of Reaction.—The dependence of the rate of reaction upon the acidity function, as well as the effect of electron-withdrawing substituents in the benzenediazo residue of substrates resulting in decreased $k_{obs.}$ values, are consistent with a mechanism in which the slow step is unimolecular decomposition of the protonated substrate, DEH^+, to the coupling entity, the diazonium ion, D^+, which instantly reacts with β-naphthol to give products. The rate of loss of the sum of the equilibrium concentrations of DE and DEH^+ is represented by equation (4) where k is the rate constant for the slow step (2) and $f^{\ddagger}$ is the activity coefficient of the transition state for that step.

$$DE + H^+ \rightleftharpoons DEH^+ \text{ (fast, pre-equilibrium)} \quad (1)$$

$$DEH^+ \xrightarrow{k} D^+ + CH_3OH \text{ (slow)} \quad (2)$$

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

$$\frac{-d(c_{DE} + c_{DEH^+})}{dt} = kc_{DEH^+}\left(\frac{f_{DEH^+}}{f^{\ddagger}}\right) \quad (4)$$

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 ionisation constant K_{DEH^+} of DEH^+, leads to equation (6). The hydrogen ion activity (a_{H^+}) can be expressed in terms of the Hammett acidity function [equation (7)] in which B represents any neutral base. Substitution in equation (6) for $a_{H^+} = h_0 f_{BH^+}/f_B$,[16] leads to equation (8).

$$k_{obs.} = -\left(\frac{1}{c_{DE} + c_{DEH^+}}\right)\frac{d(c_{DE} + c_{DEH^+})}{dt} \quad (5)$$

$$k_{obs.} = \left(\frac{c_{DE}}{c_{DE} + c_{DEH^+}}\right)\frac{k}{K_{DEH^+}}\frac{a_{H^+}f_{DE}}{f^{\ddagger}} \quad (6)$$

$$H_0 = -\log h_0 = -\log\left(\frac{a_{H^+}f_B}{f_{BH^+}}\right) \quad (7)$$

$$k_{obs.} = \left(\frac{c_{DE}}{c_{DE} + c_{DEH^+}}\right)\frac{k}{K_{DEH^+}}h_0\frac{f_{DE}f_{BH^+}}{f_B f^{\ddagger}} \quad (8)$$

If $h_0 \ll K_{DEH^+}$, whereas $H_0 \gg pK_{DEH^+}$, equilibrium (1) lies practically entirely on the left-hand side and $c_{DEH^+} \ll c_{DE}$. In consequence, equation (8) is transformed to (9) the logarithmic derivation of which is (10).

$$k_{obs.} = \frac{k}{K_{DEH^+}}h_0\frac{f_{DE}f_{BH^+}}{f_B f^{\ddagger}} \quad (9)$$

$$\log k_{obs.} = -H_0 + \log\left(\frac{k}{K_{DEH^+}}\right) + \log\frac{f_{DE}f_{BH^+}}{f_B f^{\ddagger}} \quad (10)$$

It follows from equation (10) that log $k_{obs.}$ parallels H_0,[17] if the activity coefficient term in equation (10) is independent of the medium, with the consequence that log $k_{obs.} + H_0$ = constant.

The relatively small deviations from this relationship apparent in the Table are not surprising, since it has been shown that the Hammett acidity function is not generally applicable to the protonation equilibria of structurally different indicators.[18] Because of their suitable physical properties, the nitroanilines used in the determinations of H_0 are quite different in nature from the diazo ethers involved in this reaction.

It may therefore be concluded that the diazo coupling reaction of arenediazo methyl ethers with β-naphthol proceeds in accord with the above mechanism, is agreement with the results.

Experimental

Materials.—The arylamines used in this investigation were purified by standard techniques. β-Naphthol (Eastman Kodak) was recrystallised by dissolving in benzene, filtering, and precipitating carefully from light petroleum (b.p. 60—80 °C), m.p. 123—124 °C.[19] Dioxane was purified by treatment with sodium, b.p. 101 °C at 760 mmHg, m.p. 12 °C.[20] Ethanol (B.D.H. absolute alcohol) was dehydrated with magnesium ethoxide. The method of Manske was employed to remove the last trace of water from ethanol.[21] Propan-2-ol (Eastman Kodak White Label) was refluxed over Mg and distilled at atmospheric pressure, b.p. 82.2 °C.[22] Acid solutions were prepared by passing hydrogen chloride, obtained by dropping concentrated hydrochloric acid (AnalaR) on concentrated sulphuric acid and dried over phosphoric oxide, into the solvent, and then diluting as required. HCl concentrations were determined by titration with sodium borate.[23] All solutions were made up immediately before use and carefully protected from moisture.

Isodiazoates from aniline, *p*-chloro-, *p*-bromo-, and *p*-cyanoaniline were prepared by Schraube and Schmidt's method,[24] and were crystallised by dissolving in 95% ethanol at 40—50 °C, filtering, and precipitating carefully from ether. Sodium *m*- and *p*-nitrobenzeneisodiazoates were prepared and purified as previously described.[9]

Methyl Ethers.—The arenediazo methyl ethers were prepared according to the method of Pechmann and Frobenius.[1] Benzenediazo methyl ether (**2a**) was prepared from silver benzeneisodiazoate and methyl iodide, as a yellow oil.[2] *p*-Bromobenzenediazo methyl ether (**2b**) was similarly prepared from silver *p*-bromobenzeneisodiazoate and methyl iodide. The product was obtained as a yellowish brown oil.[2] Likewise, *p*-nitrobenzenediazo methyl ether (**2f**) was prepared from silver *p*-nitrobenzeneisodiazoate and methyl iodide, crystallised from ligroin (b.p. 80—120 °C), and dried *in vacuo* at room temperature for 8 h, m.p. 82 °C (decomp.), (lit.[2] 82 °C).

p-*Chlorobenzenediazo methyl ether* (**2c**). Silver *p*-chlorobenzeneisodiazoate (10.5 g, 0.04 mol) was suspended in dry ether (60 ml) and the mixture cooled to −15 °C. Methyl iodide (7 g, 0.05 mol) was then added, and the mixture was stirred in the dark for 24 h at −15 °C. Silver iodide and unchanged silver *p*-chlorobenzeneisodiazoate were removed by filtration. The ether was removed at reduced pressure, and the residual oil was run through a 9 cm × 6.5 cm column of silica gel using chloroform as eluant. The chloroform was removed under vacuum and the product was better used without distillation (4.1 g; pale yellow oil) (Found: C, 49.3; H, 4.1; Cl, 20.6; N, 16.6. $C_7H_7ClN_2O$ requires C, 49.2; H, 4.1; Cl, 20.8; N, 16.4%).

Compounds (**2d** and **e**) were prepared by Bamberger's procedure,[2] recrystallised three times from ether–pentane, and dried *in vacuo* at room temperature for 8—10 h before use.

p-*Cyanobenzenediazo methyl ether* (**2d**) formed yellow needles, m.p. 75—76 °C (Found: C, 59.5; H, 4.4; N, 26.1. $C_8H_7N_3O$ requires C, 59.6; H, 4.35; N, 26.1%).

m-*Nitrobenzenediazo methyl ether* (**2e**) was isolated as fine yellow crystals, m.p. 44 °C (Found: C, 46.5; H, 3.8; N, 23.2. $C_7H_7N_3O_3$ requires C, 46.3; H, 3.9; N, 23.2%).

Diazo Coupling of Arenediazo Methyl Ethers.—Diazo coupling of benzene-, *p*-bromobenzene-, *p*-chlorobenzene-, *p*-cyanobenzene-, *m*-nitrobenzene-, and *p*-nitrobenzene diazo methyl ether (0.005 mol) with β-naphthol in hydrochloric acid solutions of ethanol gave the corresponding azo dyes in quantitative yield: benzeneazo-, m.p. 134 °C;[25] *p*-bromobenzeneazo-, m.p. 172 °C;[26] *p*-chlorobenzeneazo-, m.p. 160 °C;[27] *p*-cyanobenzeneazo-, m.p. 237 °C;[28] *m*-nitrobenzeneazo-, m.p. 194 °C;[29] and *p*-nitrobenzeneazo-naphth-2-ol, m.p. 250 °C.[30]

Kinetic Measurements.—Rates of reaction were determined by spectrophotometric analysis for azo dyes using a Unicam SP 600 spectrophotometer. Mixtures were made up in stoppered volumetric flasks (100 ml) maintained at 25 °C in a thermostatted water-bath. Solutions of β-naphthol and hydrochloric acid in the required solvent were placed in the flask and kept for 20 min to reach the required temperature. The diazo ether solutions were freshly prepared each day. A stock solution of the diazo ether under investigation was prepared by dissolving the required amount in 100 ml of solvent, so that 1 ml of this solution when diluted to 100 ml gave the required concentration. Measurements were started as the diazo ether solutions were pipetted into the stoppered flask which was vigorously shaken until the contents were homogeneous. This required < 8 s. Samples of the solution were withdrawn at intervals and optical densities were determined at the absorption maxima for the dyes (Table). The reaction was followed until no further change in the optical density was apparent, and the concentration of the corresponding dye for each compound investigated was calculated. In every case, the final optical density agreed to within ±2% of the value expected for 100% reaction estimated from the calibration curves of authentic samples. All runs were arranged under pseudo-first-order conditions, and pseudo-first-order rate constants ($k_{\text{obs.}}$) were obtained from plots of log ($c_{\text{DE}_0}/c_{\text{DE}_t}$) *versus* time. Therefore, $k_{\text{obs.}} = (2.3/t) \log (c_{\text{DE}_0}/c_{\text{DE}_t})$. The rate constants reported are mean values of duplicate runs and are reproducible to within ±4%. [Independent checks of the stability of the azo dyes (**3**) in the reaction media were made.]

Concentration Ranges.—The required concentration [*e.g.* 4.8×10^{-5}M for (**2c**)] of the diazo ethers investigated was fixed by the need for a change of optical density of *ca.* 0.9 in the 1 cm cell. β-Naphthol was required to be in large excess, and its concentration (4.5×10^{-3}M) remained constant throughout. The maximum concentration (1M) of HCl was fixed by the maximum rate which could conveniently be measured. In all cases at least a 400-fold excess of HCl was used.

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