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KINETICS AND MECHANISM OF THE DIAZO COUPLING REACTION OF 1-ARYL-3,3-DIETHYLTRIAZINES WITH ß-NAPHTHOL IN ACID SOLUTIONS

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ABSTRACT. A series of *m*- and *p*-substituted 1-aryl-3,3-diethyltriazines have been prepared. The kinetics of formation of azo dyes from these triazines and ß-naphthol in presence of acids were studied in solutions of benzene and ethanol at 25°. For a series of six acids of different acid strengths, pseudo-first-order rate constants were obtained, and the reaction was found to be of third order, first order in triazine, and second order in acid. The second order kinetics in acid (k) were linearly correlated with the Hammett substituent constant (σ_x). The verification of the linear relationship between the second order kinetics in acid and the acid strengths (K_a) in benzene and ethanol is satisfactory. The kinetic results support a mechanism in which the slow step is bimolecular decomposition of the protonated triazine, TH^+, with an acid, HA, to the coupling entity, the diazonium ion, ArN_2^+, which instantly reacts with ß-naphthol to give the azo dye.

INTRODUCTION

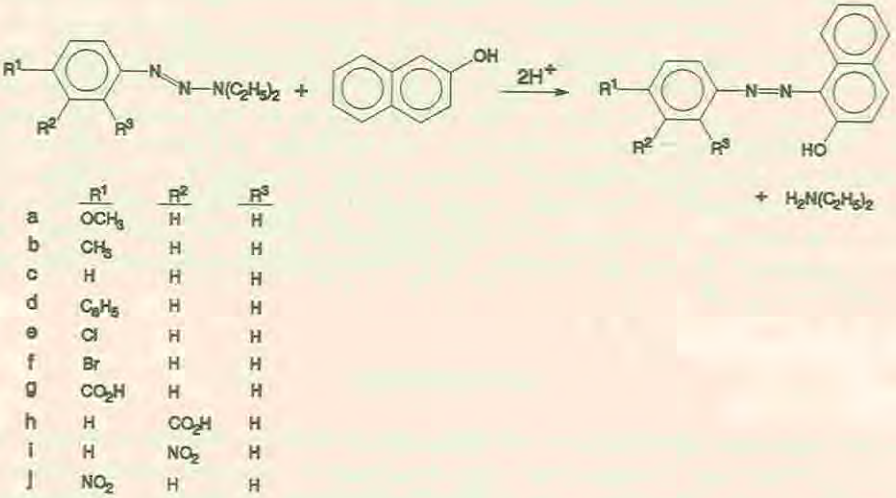
The azo dyes and pigments form the largest group of all the synthetic colorants and play a prominent part in almost every type of application. For textile printing, mixtures of stabilized diazo compounds and coupling components are required. Isodiazoates [1], arenediazophenyl sulfides [2], and arenediazomethyl ethers [3,4] were introduced as examples of stabilized diazo compounds.

Arenediazoamino compounds (triazines) can also be used as passive stabilized diazo compounds from which the original diazonium ion can be regenerated by suitable treatment [5]. The triazines are of importance as Rapidogen Dyes (IG) and are used in printing pastes [6]. Moreover, they have been utilized in rubber industry and in motor fuel as anti-knock agents for diesel fuel [7]. Triazines (particularly the 3,3-dialkyl derivatives) are potent carcinogens [8] and are also alleged to have insecticidal properties [9].

The 1-aryl-3,3-dialkyltriazines have now been prepared from *m*- & *p*-aminobenzoic acids, *p*-aminobiphenyl, aniline and substituted anilines. Of these, 3,3-diethyl-1-phenyltriazine has been described by Vignon and Simonet [10]. The compounds were prepared, usually in excellent yield, by coupling diazotised anilines with diethylamine in the presence of sodium carbonate. Such triazines, which may be liquids or solids, are stable in neutral or alkaline media but decompose into the diazo- and the diethylamine salt in the presence of acids.

The diazo coupling reaction of 1-aryl-3,3-diethyltriazines (**1a-j**) with ß-naphthol in benzene and ethanol solutions and in the presence of acids gave almost quantitative yields of the azo dyes (**2a-j**).

The diazo coupling reaction of the triazines (**1**) with ß-naphthol in benzene and ethanol was monitored spectrophotometrically at 480 nm (the absorbtion maximum of the corresponding dye (**2**)). No reaction was observed in dry organic solvents. Acids accelerate the production of colour. Accordingly, the effects of acetic, formic, chloroacetic, oxalic, picric and nitric acids in ethanol solutions, and of the first three acids in benzene solutions, on the reaction rate were examined at 25°. Reactions were carried out under pseudo-first-order conditions and it was observed that the reaction showed no marked variation in the rate of decomposition of 1-aryl-3,3-diethyltriazines with varying concentrations of ß-naphthol (Fig. 1).



	R^1	R^2	R^3
a	OCH_3	H	H
b	CH_3	H	H
c	H	H	H
d	C_6H_5	H	H
e	Cl	H	H
f	Br	H	H
g	CO_2H	H	H
h	H	CO_2H	H
i	H	NO_2	H
j	NO_2	H	H

The reaction between each compound (**1**) and ß-naphthol in the two different solvents at the lowest and highest concentrations of the above mentioned acids was carried out to isolate the products. In every case, the product was the corresponding dye (**2**). The rate of formation of the dye followed at λ_{max} was thus assumed to be proportional to the concentration of the reacted triazine, T. In all cases the extent of the reaction was not less than 98%.

RESULTS AND DISCUSSION

Reaction rates. Each system showed good first order behaviour over three half-lives. Typical first order plots are shown in Fig. 2. Values of k_{obs} obtained under a variety of conditions are given in Table 1. For each compound, the values appeared to be sensitive to the acid concentrations over the range used (form 0.05 to 7.5 M on going from nitric to acetic acid) and to strength of the acid used. Kinetic studies were carried out at five different concentrations for each acid with all the triazines examined (**1a-j**), the initial triazine concentrations being *ca.* 10^{-5} M throughout (see Table 1).

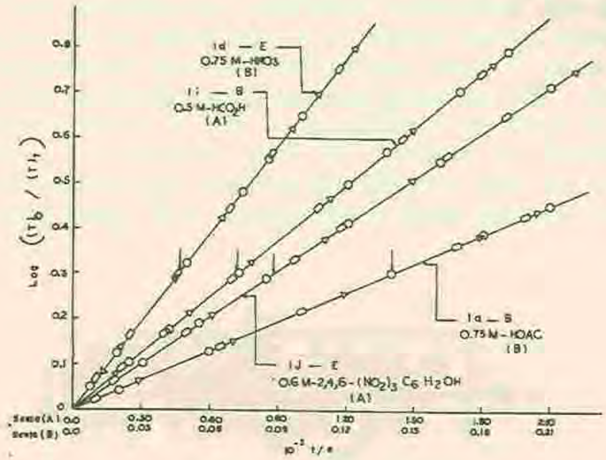


Fig. 1. Effect of change of ß-naphthol concentration on the overall rate of decomposition of 1-aryl-3,3-diethyltriazines at 25°. 10^4[ß-naphthol] ○, 45; □, 65; △, 650. B = benzene, E = ethanol. Arrows mark one half-life.

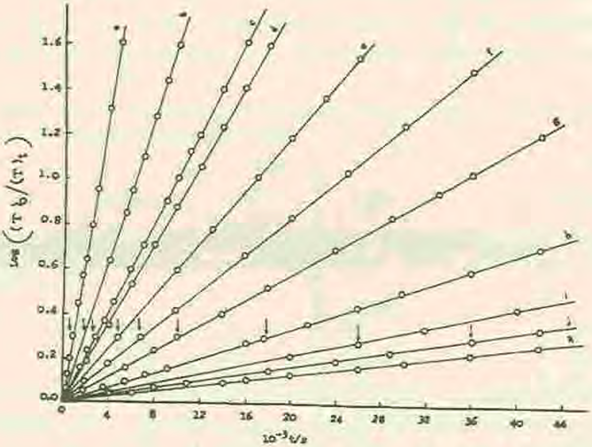


Fig. 2. Representative pseudo-first-order kinetic plots for the diazo coupling reaction of 1-aryl-3,3-diethyltriazines with ß-naphthol in benzene [B] and ethanol [E] at 25°. Reactions were carried out at constant concentration of triazines (Table 1), ß-naphthol (4.5 X 10^{-3}) and variable concentration of acids: a - (**1b**)-E, 0.75 M $(CO_2H)_2$; b - (**1e**)-E, 0.2 M 2,4,6-$(NO_2)_3C_6H_2OH$; c - (**1a**)-E, 1.5 M HCO_2H; d - (**1h**)-B, 0.35 M HOAc; e - (**1f**)-B, 0.1 M HCO_2H; f - (**1c**)-B, 0.04 M $ClCH_2CO_2H$; g - (**1d**)-E, 0.05 M HNO_3; h - (**1j**)-E, 5.0 M HOAc; i - (**1g**)-E, 1.0 M HCO_2H; j - (**1j**)-E, 0.8 M $ClCH_2CO_2H$; k - (**1l**)-B, 0.04 M $ClCH_2CO_2H$. Arrows mark one half-life.

The values of k_{obs} are markedly affected by the nature of the solvent (Table 1). For each compound, the relative magnitudes of k_{obs} in benzene and ethanol at any acid concentration mostly increase in the order ethanol < benzene.

In spite of the fact that the reaction was catalyzed by acid, a non-linear relationship was catalyzed by acid, a non-linear relationship was apparent. The measured k_{obs} values did not show a linear function to the first power of the acid concentration (Table 1). Also shown in Table 1 are the third-order rate constants as a function of acid concentration. The correlation between k_{obs} and $[HA]^2$ for the acid-catalyzed decomposition of 3,3-diethyl-1-phenyltriazine and its substituted derivatives in benzene and ethanol is evident. For each compound, a variation of acid concentration over an order of magnitude produced approximately the same rate constant ($l^2mol^{-2}s^{-1}$) for each series of acids used in both organic solvents.

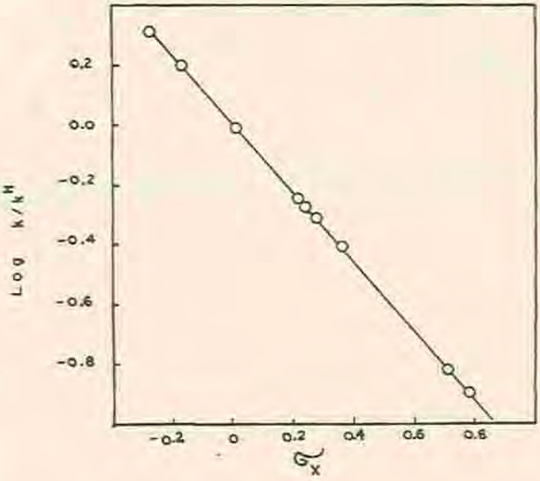


Fig. 3. Plot of log k/k^{H} for the acid-catalyzed decomposition of *m*- and *p*-substituted triazines (**1a** - **j**) at a constant acid concentration of 1 M, *versus* Hammett σ_x values of the substituents. Slope is -1.15.

In addition, the data listed in Table 1 included ten orders of magnitude in reactivity and ranged from **1j** (least reactive) to **1a** (most reactive). The other eight in order of decreasing reactivity were **1b** > **1c** > **1d** > **1e** > **1f** > **1g** > **1h** > **1i**. The activities of the triazines (**1a-j**, Fig. 3) at an acid concentration of 1 M are correlated with the Hammett substituent constant (σ_x). The measured rates increase for electron donating substituents on the aryl portion of the triazines. Electron-withdrawing substituents decrease the basicities of compounds **1a-j**. The value of the Hammett reaction constant (ρ) [13] is -1.15 (Fig. 3) and suggests an early transition state [14]. The fact that the reaction is of second order kinetics with respect to the acids used is clearly inconsistent with proton transfer being the rate-determining step.

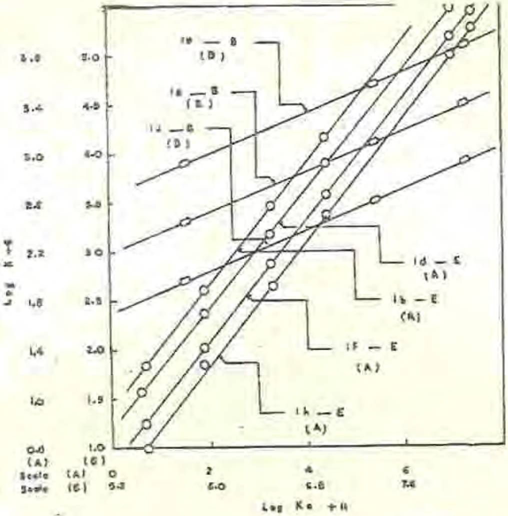


Fig. 4. Correlation of acid dissociation constants (K_a, Table 2) with rate constants (k, Table 1) for the diazo coupling reaction of some triazines with ß-naphthol at 25°. B = benzene, E = ethanol.

The data shown in Table 1 demonstrate that reaction rates of the triazine decompositions (using acetic, formic, and chloroacetic acids) are markedly affected by the nature of the solvent, and increase 10^2-fold when ethanol (ϵ = 24.5) was replaced by benzene (ϵ = 2.3). This solvent effect may be explained by comparing the kinetic results with the relative strengths of the three acids in the two solvents.

Table 1. Rate constants for the acid-catalyzed diazo coupling reaction of 1-aryl-3,3-diethyltriazines (**1a - j**) with ß-naphthol in benzene and ethanol at 25°[a].

Compound	$\frac{[HA]}{M}$	$\frac{10^5 k'_{obs}}{s^{-1}}$	$\frac{10^5 k}{l^2 mol^{-2} s^{-1}}$	$\frac{[HA]}{M}$	$\frac{10^5 k'_{obs}}{s^{-1}}$	$\frac{10^5 k}{l^2 mol^{-2} s^{-1}}$
	Solvent, Ethanol					
	HOAc			$(CO_2H)_2$		
	1.00	2.41	2.41	0.50	43.60	174.4
	2.50	15.13	2.42	0.75	97.78	174.6
	3.50	29.52	2.41	1.25	272.22	174.5
	5.00	60.00	2.40	2.00	697.60	174.4
	7.50	136.13	2.42	3.25	1841.70	174.4
	HCO_2H			2,4,6-$(NO_2)_3C_6H_2OH$		
	1.00	10.24	10.24	0.08	21.76	3400
	1.50	23.10	10.27	0.12	48.99	3402
(1a)[b]	2.50	64.13	10.26	0.20	136.00	3400
	3.50	125.69	10.26	0.40	544.32	3402
	5.00	255.75	10.23	0.60	1224.36	3401
	$ClCH_2CO_2H$			HNO_3		
	0.40	7.34	45.90	0.05	13.79	5516
	0.80	29.38	45.90	0.10	55.18	5518
	1.20	66.24	46.00	0.25	345.00	5520
	1.60	117.25	45.80	0.50	1379.50	5518
	2.40	264.38	45.90	0.75	3102.70	5516

(1b)[c]	HOAc			$(CO_2H)_2$		
	1.00	1.88	1.88	0.50	34.25	137.0
	2.50	11.87	1.90	0.75	77.05	137.6
	3.50	23.00	1.88	1.25	213.75	137.0
	5.00	46.75	1.87	2.00	546.00	146.5
	7.50	104.63	1.86	3.25	1436.20	136.0
	HCO_2H			$2,4,6\text{-}(NO_2)_3C_6H_2OH$		
	1.00	7.98	7.98	0.08	16.96	2650
	1.50	17.93	7.97	0.12	38.13	2648
	2.50	50.06	8.01	0.20	106.16	2654
	3.50	97.75	7.98	0.40	424.00	2650
	5.00	199.00	7.96	0.60	954.72	2652
	$ClCH_2CO_2H$			HNO_3		
	0.40	5.73	35.81	0.05	10.82	4328
	0.80	22.90	35.78	0.10	43.06	4306
	1.20	51.58	35.82	0.25	267.25	4276
	1.60	91.60	35.78	0.50	1076.00	4304
	2.40	206.20	35.80	0.75	2409.70	4284
(1c)[d]	HOAc			$(CO_2H)_2$		
	1.00	1.18	1.18	0.50	21.38	85.5
	2.50	7.38	1.18	0.75	47.90	85.5
	3.50	14.38	1.19	1.25	133.07	85.3
	5.00	29.25	1.17	2.00	342.00	85.5
	7.50	66.94	1.19	3.25	905.00	85.7
	HCO_2H			$2,4,6\text{-}(NO_2)_3C_6H_2OH$		
	1.00	5.02	5.02	0.08	10.66	1666
	1.50	11.28	5.01	0.12	24.02	1668
	2.50	31.38	5.02	0.20	66.80	1670
	3.50	61.61	5.03	0.40	266.24	1664
	5.00	125.50	5.02	0.60	600.12	1667
	$ClCH_2CO_2H$			HNO_3		
	0.40	3.59	22.40	0.05	6.75	2700
	0.80	14.46	22.60	0.10	27.10	2710
	1.20	32.40	22.50	0.25	169.00	2704
	1.60	57.60	22.50	0.50	677.00	2708
	2.40	129.60	22.50	0.75	1520.40	2703
(1d)[d]	HOAc			$(CO_2H)_2$		
	1.00	1.15	1.15	0.50	20.92	83.68
	2.50	7.25	1.16	0.75	46.87	83.70
	3.50	14.21	1.16	1.25	140.57	83.70
	5.00	29.25	1.17	2.00	334.84	83.71
	7.50	65.25	1.16	3.25	883.87	83.70
	HCO_2H			$2,4,6\text{-}(NO_2)_3C_6H_2OH$		
	1.00	4.94	4.94	0.08	10.40	1634
	1.50	11.07	4.92	0.12	23.52	1638
	2.50	30.75	4.92	0.20	65.44	1636
	3.50	60.03	4.90	0.40	261.60	1635
	5.00	123.25	4.93	0.60	588.24	1634
	$ClCH_2CO_2H$			HNO_3		
	0.40	3.54	22.13	0.05	6.62	2648
	0.80	14.15	22.11	0.10	26.50	2650
	1.20	31.81	22.09	0.25	165.75	2652
	1.60	56.53	22.08	0.50	662.00	2648
	2.40	127.30	22.10	0.75	1495.00	2658
(1e)[d]	HOAc			$(CO_2H)_2$		
	1.00	0.65	0.65	0.50	11.75	47.0
	2.50	4.00	0.64	0.75	26.21	46.8
	3.50	7.96	0.65	1.25	73.47	47.1
	5.00	16.50	0.66	2.00	187.60	46.9
	7.50	36.56	0.65	3.25	497.37	47.1
	HCO_2H			$2,4,6\text{-}(NO_2)_3C_6H_2OH$		
	1.00	2.75	2.75	0.08	5.87	917.2
	1.50	6.23	2.77	0.12	13.22	918.1
	2.50	17.25	2.76	0.20	36.80	920.0
	3.50	33.93	2.77	0.40	146.90	918.0
	5.00	68.75	2.75	0.60	330.12	917.0
	$ClCH_2CO_2H$			HNO_3		
	0.40	1.98	12.38	0.05	3.72	1488
	0.80	7.94	12.41	0.10	14.90	1490
	1.20	17.88	12.42	0.25	92.88	1486
	1.60	31.73	12.39	0.50	372.25	1489
	2.40	71.42	12.40	0.75	837.00	1488

(**1f**)[c]	HOAc			$(CO_2H)_2$		
	1.00	0.63	0.63	0.50	11.55	46.20
	2.50	4.00	0.64	0.75	25.85	46.16
	3.50	7.72	0.63	1.25	72.13	46.24
	5.00	15.50	0.62	2.00	184.72	46.18
	7.50	36.00	0.64	3.25	488.08	46.22
	HCO_2H			2,4,6-$(NO_2)_3C_6H_2OH$		
	1.00	2.71	2.71	0.08	5.76	900.00
	1.50	6.10	2.71	0.12	12.96	900.00
	2.50	17.06	2.73	0.20	36.04	901.00
	3.50	33.32	2.72	0.40	143.84	899.00
	5.00	67.75	2.71	0.60	324.00	900.00
	$ClCH_2CO_2H$			HNO_3		
	0.40	1.95	12.19	0.05	3.65	1460
	0.80	7.82	12.22	0.10	14.62	1462
	1.20	17.54	12.18	0.25	91.25	1460
	1.60	31.23	12.20	0.50	365.25	1461
	2.40	70.33	12.21	0.75	822.37	1462
(**1g**)[c]	HOAc			$(CO_2H)_2$		
	1.00	0.58	0.58	0.50	10.47	41.88
	2.50	3.63	0.58	0.75	23.46	41.89
	3.50	7.35	0.60	1.25	65.33	41.88
	5.00	14.75	0.59	2.00	167.68	41.92
	7.50	32.06	0.57	3.25	422.67	41.92
	HCO_2H			2,4,6-$(NO_2)_3C_6H_2OH$		
	1.00	2.47	2.47	0.08	5.23	817.20
	1.50	5.58	2.48	0.12	11.76	816.67
	2.50	15.37	2.46	0.20	32.68	817.00
	3.50	30.01	2.45	0.40	130.69	816.81
	5.00	61.25	2.45	0.60	294.12	817.00
	$ClCH_2CO_2H$			HNO_3		
	0.40	1.76	11.00	0.05	3.32	1328
	0.80	7.06	11.03	0.10	13.26	1326
	1.20	15.90	11.04	0.25	82.88	1326
	1.60	28.24	11.03	0.50	331.75	1327
	2.40	63.59	11.04	0.75	745.32	1325
(**1h**)[d]	HOAc			$(CO_2H)_2$		
	1.00	0.39	0.39	0.50	8.32	33.28
	2.50	2.44	0.39	0.75	18.64	33.29
	3.51	4.90	0.40	1.25	51.93	33.29
	5.00	9.50	0.38	2.00	133.20	33.30
	7.50	22.50	0.40	3.25	351.65	33.30
	HCO_2H			2,4,6-$(NO_2)_3C_6H_2OH$		
	1.00	1.97	1.97	0.08	4.16	650.00
	1.50	4.41	1.96	0.12	9.36	650.00
	2.50	12.31	1.97	0.20	25.94	648.50
	3.50	24.01	1.96	0.40	104.21	651.30
	5.00	49.00	1.96	0.60	233.93	649.80
	$ClCH_2CO_2H$			HNO_3		
	0.40	1.39	8.69	0.05	2.63	1052
	0.80	5.57	8.70	0.10	10.56	1056
	1.20	12.51	8.69	0.25	66.00	1056
	1.60	22.30	8.71	0.50	263.80	1055
	2.40	50.11	8.70	0.75	594.00	1056
(**1i**)[d]	HOAc			$(CO_2H)_2$		
	1.00	0.18	8.18	0.50	3.21	12.84
	2.50	1.12	0.18	0.75	7.18	12.82
	3.50	2.21	0.18	1.25	19.97	12.80
	5.00	4.48	0.18	2.00	51.20	12.80
	7.50	10.12	0.18	3.25	135.38	12.82
	HCO_2H			2,4,6-$(NO_2)_3C_6H_2OH$		
	1.00	0.75	0.75	0.08	1.60	250.00
	1.50	0.75	0.75	0.12	3.58	248.60
	2.50	0.74	0.74	0.20	9.95	248.80
	3.50	0.73	0.73	0.40	39.81	248.80
	5.00	0.75	0.75	0.60	90.00	250.00
	$ClCH_2CO_2H$			HNO_3		
	0.40	0.54	3.38	0.05	1.02	408
	0.80	2.18	3.41	0.10	4.06	406
	1.20	4.90	3.40	0.25	25.44	407
	1.60	8.76	3.42	0.50	101.50	406
	2.40	19.58	3.40	0.75	228.37	406

(1j)[d]	HOAc			$(CO_2H)_2$		
	1.00	0.15	0.15	0.50	2.77	11.08
	2.50	0.94	0.15	0.75	6.21	11.09
	3.50	1.84	0.15	1.25	17.33	11.11
	5.00	3.80	0.15	2.00	44.40	11.10
	7.50	8.44	0.15	3.25	117.22	11.10
	HCO_2H			2,4,6-$(NO_2)_3C_6H_2OH$		
	1.00	0.64	0.64	0.08	1.39	217.20
	1.50	1.46	0.65	0.12	3.13	217.40
	2.50	4.00	0.64	0.20	8.68	217.00
	3.50	7.96	0.65	0.40	34.69	216.80
	5.00	16.25	0.65	0.60	78.20	217.20
	$ClCH_2CO_2H$			HNO_3		
	0.40	0.46	2.88	0.05	0.88	352
	0.80	1.84	2.88	0.10	3.52	352
	1.20	4.19	2.91	0.25	21.94	351
	1.60	7.42	2.90	0.50	88.00	352
	2.40	16.70	2.90	0.75	197.44	351
(1a)[b]	Solvent, Benzene					
	HOAc			$ClCH_2CO_2H$		
	0.10	8.70	870	0.04	19.68	12300
	0.25	54.50	872	0.08	79.10	12360
	0.35	106.00	865	0.12	177.70	12340
	0.50	217.50	870	0.16	315.40	12320
	0.75	492.20	875	0.24	710.20	12330
	HCO_2H					
	0.10	51.10	5110			
	0.15	115.20	5120			
	0.25	320.00	5120			
	0.35	628.40	5130			
	0.50	1279.5	5118			
(1b))[c]	HOAc			$ClCH_2CO_2H$		
	0.10	6.81	681	0.04	15.30	9563
	0.25	42.50	680	0.08	61.31	9580
	0.35	83.30	680	0.12	137.90	9576
	0.50	170.50	682	0.16	245.25	9580
	0.75	380.81	677	0.24	550.10	9550
	HCO_2H					
	0.10	39.80	3980			
	0.15	89.90	3996			
	0.25	250.00	4000			
	0.35	488.80	3990			
	0.50	996.50	3986			
(1c)[d]	HOAc			$ClCH_2CO_2H$		
	0.10	4.27	427.00	0.04	9.66	6038
	0.25	26.68	426.90	0.08	38.53	6020
	0.35	52.31	427.00	0.12	86.80	6028
	0.50	106.70	426.80	0.16	154.20	6023
	0.75	240.30	427.20	0.24	347.30	6030
	HCO_2H					
	0.10	25.07	2507			
	0.15	56.52	2512			
	0.25	156.75	2508			
	0.35	308.00	2514			
	0.50	627.50	2510			
(1d)[d]	HOAc			$ClCH_2CO_2H$		
	0.10	4.20	420	0.04	9.44	5900
	0.25	26.38	422	0.08	37.76	5900
	0.35	50.96	416	0.12	85.00	5903
	0.50	103.80	415	0.16	151.20	5906
	0.75	234.60	417	0.24	339.00	5885
	HCO_2H					
	0.10	24.56	2456			
	0.15	55.31	2458			
	0.25	153.88	2462			
	0.35	301.84	2464			
	0.50	615.00	2460			

(1e)^d	HOAc			$ClCH_2CO_2H$		
	0.10	2.36	236	0.04	5.29	3306
	0.25	14.75	236	0.08	21.15	3305
	0.35	28.67	234	0.12	47.72	3314
	0.50	58.75	235	0.16	84.70	3309
	0.75	131.60	234	0.24	190.94	3315
	HCO_2H					
	0.10	13.78	1378			
	0.15	30.94	1375			
	0.25	86.38	1382			
	0.35	169.05	1380			
	0.50	346.00	1384			
(1f)^e	HOAc			$ClCH_2CO_2H$		
	0.10	2.32	232	0.04	5.19	3244
	0.25	14.50	232	0.08	20.80	3250
	0.35	27.93	228	0.12	46.87	3255
	0.50	57.50	230	0.16	83.23	3251
	0.75	128.25	228	0.24	187.14	3249
	HCO_2H					
	0.10	13.46	1346			
	0.15	30.37	1350			
	0.25	84.25	1348			
	0.35	165.62	1352			
	0.50	338.00	1352			
(1g)^e	HOAc			$ClCH_2CO_2H$		
	0.10	2.08	208	0.04	4.37	2956
	0.25	13.06	209	0.08	18.88	2950
	0.35	25.48	208	0.12	42.51	2952
	0.50	52.50	210	0.16	75.39	2945
	0.75	118.13	210	0.24	169.80	2948
	HCO_2H					
	0.10	12.30	1230			
	0.15	27.80	1236			
	0.25	76.75	1228			
	0.35	150.65	1230			
	0.50	307.00	1228			
(1h)^d	HOAc			$ClCH_2CO_2H$		
	0.10	1.67	167	0.04	3.75	2344
	0.25	10.50	168	0.08	15.04	2350
	0.35	20.47	167	0.12	33.70	2340
	0.50	42.50	170	0.16	60.29	2355
	0.75	92.81	165	0.24	135.48	2352
	HCO_2H					
	0.10	9.82	982			
	0.15	22.00	978			
	0.25	61.25	980			
	0.35	119.81	978			
	0.50	245.50	982			
(1i)^d	HOAc			$ClCH_2CO_2H$		
	0.10	0.65	65.0	0.04	1.45	996
	0.25	4.10	65.6	0.08	5.79	905
	0.35	7.94	64.8	0.12	13.00	903
	0.50	16.15	64.6	0.16	23.22	907
	0.75	36.56	65.0	0.24	51.84	900
	HCO_2H					
	0.10	3.82	382			
	0.15	8.55	380			
	0.25	24.00	384			
	0.35	46.31	378			
	0.50	95.45	382			
(1j)^d	HOAc			$ClCH_2CO_2H$		
	0.10	0.55	55	0.04	1.25	781
	0.25	3.56	57	0.08	5.01	783
	0.35	6.62	54	0.12	11.30	785
	0.50	13.75	55	0.16	20.04	783
	0.75	30.38	54	0.24	45.10	783
	HCO_2H					
	0.10	3.25	325			
	0.15	7.29	324			
	0.25	20.25	324			
	0.35	39.45	322			
	0.50	81.50	326			

^{a}Concnetration varies from 3.5 X 15^{-5} M [for (1j)] to 5.5 X 10^{-5} M [for (1a)]. $^b\lambda_{max}$ 470 nm. $^c\lambda_{max}$ 470 nm. $^d\lambda_{max}$ 470 nm. $^e\lambda_{max}$ 470 nm. ^{f}Average of atleast two runs, rates were reproducible to ± 4%.

The pK_a values of the various acids used in water, benzene, and ethanol [15,16] are given in Table 2. The data demonstrate that even in a solvent with as low a constant as benzene, the measured acid strength [15] of chloroacetic, formic and acetic acid, place these acids in the same order as in water. The acidity of the foregoing acids is *ca* 10^5 times less in ethanol than in water, whereas, for picric acid, the increase in pK_a in passing form water to ethanol is 2 units (i.e. 100 fold) less than for other carboxylic acids. The order of strength of the six acids used in ethanol is:

$$HNO_3 > 2,4,6\text{-}(NO_2)_3C_6H_2OH > (CO_2H)_2 > ClCH_2CO_2H > HCO_2H > CH_3CO_2H$$

The rates of the diazo coupling of the triazines **1a-j** with ß-naphthol in the presence of acids (Table 1) are consistently higher in benzene than in ethanol. The ratios, $k_{ethanol}/k_{benzene}$, at 1 M acid concentration are: 0.003, 0.002, and 0.004 for acetic, formic and chloroacetic acid, respectively. Fig. 4 is the logarithmic plot of k ($l^2mol^{-2}s^{-1}$) *versus* K_a. A linear relation is observed between k (Table 1) and K_a (Table 2) for the acid-catalyzed decomposition of triazines in benzene and ethanol. Thus, decomposition of each of the triazines in acid media exhibits general acid catalysis.

Table 2. Relative acid strength in water, benzene [15], and ethanol [16].

Acid	pK_a water	pK_a benzene	pK_a ethanol
Nitric	-	-	3.57
Picric	0.80		4.00
Oxalic	1.30		6.58
Chloroacetic	2.86	2.90	7.74
Formic	3.75	3.64	9.15
Acetic	4.75	5.18	10.32

The dependence of the rate of reaction upon the square of the acid concentration, as well as the effect of electron-withdrawing substituents in the benzenediazo residue of substrate which resulted in decreased k_{obs} values, and the linear relationship between values of k and K_a in benzene and ethanol are compatible with the sequence presented in the following equations (Eq. 1-3):

$$ArN_2N(C_2H_5)_2 + HA \rightleftharpoons ArN_2N^+H(C_2H_5)_2 + A^- \qquad (1)$$

$$ArN_2N^+H(C_2H_5)_2 + HA \rightarrow ArN_2^+ + (C_2H_5)_2NH_2^+A^- \qquad (2)$$

$$ArN_2^+ + HOC_{10}H_7 - \beta + A^- \rightarrow ArN_2C_{10}H_6(OH) - \beta + HA \qquad (3)$$

The slow step (eq. (2)) is the bimolecular decomposition of the protonated substrate TH^+ (eq. (2)) to give the diazonium ion, ArN^+_2 which instantly reacts with ß-naphthol to give products. The rate of reaction, obtained by the steady-state approximation, is represented by eq. (4), where k_2 is the rate constant for the slow step.

$$Rate = \frac{k_1k_2[T][HA]^2}{k_{-1} + k_2[HA]} \qquad (4)$$

If $k_{-1} > k_2$ [HA], the reaction becomes second order in acid, and the experimental first-order rate constant (k_{obs}) is given by eq. (5).

$$k_{obs} = K[HA]^2 \qquad (5)$$

where

$$K = \frac{k_1 k_2}{k_{-1}}$$

The results obtained for the diazo coupling reaction of 1-aryl-3,3-diethyltriazines with ß-naphthol is consistent with the steps presented in the equations above.

EXPERIMENTAL

Materials. 4-Aminobiphenyl (Jansen Chimica) was crystallised from light petroleum (b.p. 40 - 60°) to a constant m.p. of 53° [17]. The other arylamines used in this investigation and ß-naphthol were purified as described in previous papers [1-3]. Diethylamine (Merck) was distilled, and the fraction boiling at 54 - 57° was collected [18]. Acetic, formic, oxalic, picric, and nitric acids were purified by standard methods and dried as mentioned earlier [1]. Chloroacetic acid for analysis (Jansen Chimica) was distilled (air condenser), and the fraction boiling at 182 - 192° was collected, which solidified on cooling (m.p. 63° [19]). Reagent grade benzene (Merck), free from thiophene [20], b.p. 79.5° was used. Absolute ethanol (BDH) was dehydrated as described before [3]. Water content was determined following Vogel's procedure [21]. Batches containing more than 0.05% water were discarded.

1-Aryl-3,3-diethyltriazines (**1a-j**). General procedure: An aqueous solution of the diazonium chloride, prepared in the usual manner from the aromatic amine (0.05 mole) was added slowly from a cooled dropping funnel to a cooled stirred mixture of diethylamine (3.7 g) and sodium carbonate (15 g) in water (50 ml). Stirring was continued for 30 min and the separated triazine was then either extracted with ether or benzene or, if solid collected by filtration. The extract was dried over caustic potash and after removal of the solvent, the residual triazine was distilled under reduced pressure. The solid triazines were recrystallised from suitable solvents (Table 3) and dried *in vacuo*. Diazo coupling of 1-aryl-3,3-diethyltriazines. Diazo coupling of 1-methoxyphenyl-,1-*p*-tolyl-, 1-phenyl-, 1-*p*-chlorophenyl-, 1-*p*-bromophenyl-, 1-*p*-carboxyphenyl-, 1-*m*-carboxyphenyl-, 1-*m*-nitrophenyl-, and 1-*p*-nitrophenyl-3,3-diethyltriazine with ß-naphthol in acid solutions of benzene and of ethanol gave in quantitative yields the corresponding azo dyes, namely *p*-methoxybenzeneazo-, m.p. 137° [22]; *p*-methylbenzeneazo-, m.p. 135° [23]; benzeneazo-, m.p. 134° (3); *p*-chlorobenzeneazo-, m.p. 160° [3]; *p*-bromobenzeneazo-, m.p. 172° [3]; *p*-carboxybenzeneazo-, m.p. 301° [2]; *m*-carboxybenzeneazo-, m.p. 242° [24]; *m*-nitrobenzeneazo-, m.p. 194° [3]; and *p*-nitrobenzeneazo-2-naphthol, m.p. 251° [3]. UV (C_2H_5OH) λ_{max} (nm): 220 - 240, 280-295, 315 - 340 [11]; IR ν_{max} (KBr) cm^{-1}: 1400, 1600 (-N=N-) [2,12]

Table 3. 1-Aryl-3,3-diethyltriazines prepared from diazonium chlorides and diethylamine following general procedure.

Substrate	Yield (%)	B.p./mm Hg or m.p.(°C)	Formula	Analytical results (%) or reference
1a	87	175-176/15	$C_{11}H_{17}N_3O$ (207.27)	Calcd.C63.74 H8.27 N20.27 Found C63.80 H8.18 N20.28
1b	85	148-150/15	$C_{11}H_{17}N_3$ (191.27)	Calcd.C69.07 H8.96 N21.97 Found C68.86 H9.12 N22.03
1c	85	155-156/20[a]	$C_{10}H_{15}N_3$ (177.24)	[10]
1d	93	28-29[b]	$C_{16}H_{19}N_3$ (253.33)	Calcd.C75.85 H7.56 N16.59 Found C75.85 H7.57 N16.59
1e	90	164-166/36	$C_{10}H_{14}ClN_3$ (211.68)	Clacd.C56.74 H6.67 N19.85 Found C56.84 H6.56 N19.76
1f	88	143-145/32	$C_{10}H_{14}BrN_3$ (256.13)	Calcd.C46.89 H5.51 N16.41 Found C46.86 H5.49 N16.40
1g	93	156-157[c]	$C_{11}H_{15}N_3O_2$ (221.25)	Calcd.C59.71 H6.83 N18.99 Found C59.74 H6.81 N18.98
1h	94	104-105[d]	$C_{11}H_{15}N_3O_2$ (221.25)	Calcd.C59.71 H6.83 N18.99 Found C59.72 H6.80 N19.00
1i	90	31-32[e]	$C_{10}H_{14}N_4O_2$ (222.24)	Calcd.C54.04 H6.35 N25.21 Found C54.18 H6.28 N25.17
1j	95	64-65[f]	$C_{10}H_{14}N_4O_2$ (222.24)	Calcd.C54.04 H6.35 N25.21 Found C54.05 H6.30 N25.25

[a] Ref. [10], b.p. 258-260° at 760 mm Hg.
[b] Buff-coloured plates from aqueous methanol.
[c] Long yellow needles from benzene/ligroin.
[d] Orange needles form benzene.
[e] Pale yellow crystals from light petroleum (40-60°).
[f] Reddish needles from benzene.

p-Biphenylazo-2-naphthol (**2d**). Diazo coupling of 1-*p*-biphenyl-3,3-diethyltriazine (0.002 mole) with ß-naphthol (0.5 g; 0.003 mole) in acid solutions of benzene and of ethanol (10 ml) resulted in the isolation of deep red needles (0.6 g; 95%), m.p. 169-170°. Found C, 81.50; H, 4.90; N, 8.65, Calcd. for $C_{22}H_{16}N_2O$ (324.36): C, 81.46; H, 4.97; N, 8.64.

Kinetic measurements. Rates of reaction were determined by spectrophotometric analysis for azo dyes using a Bausch and Lomb spectronic 21 UVD spectrophotometer. The technique used in the present study had been detailed in previous papers [3,4]. Reactions were studied under pseudo-first-order conditions, with ß-naphthol and acids in excess. The measured first-order rate constants (k_{obs}) were obtained from plots of $\log([t]_0 / [T]_t)$ *versus* time. Thus,

$$k_{obs} = (2.3 / t) \log([T]_0 / [T]_t)$$

where subscripts 0 and t refer to zero time and time t, respectively. The rate constants reported are mean values of duplicate runs and are reproducible to within ± 4 %.

Concentration ranges. The required concentration (e.g. 5.5×10^{-5} M for **1a**) of the triazines investigated was fixed by the need for a change of optical density of *ca.* 0.9 in the 10 mm cell. ß-Naphthol was required to be in large excess, and its concentration (4.5×10^{-3} M) remained constant throughout. The maximum concentration of acids (e.g. 7.5 M for acetic acid, and 0.75 M for nitric acid in ethanol solutions) was fixed by the maximum rate which could conveniently be measured. In all cases at least a 700-fold excess of acid was used.

UV spectra were measured with the spectronic 21 or a Unicam SP 600 spectrophotometer. IR spectra were recorded on a Unicam SP 1000 infrared spectrophotometer.

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