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Studies of Diazosulfides. I.[*1] A Kinetic Study of the Reaction of Diaryldiazosulfides with β-Naphthol in Alkaline Ethanol

Takashi YAMADA,[*2] Nobuo TANAKA, Takao MORISAWA,[*3]
Masao NISHIKURI and Aritsune KAJI

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto

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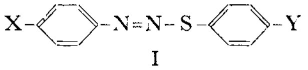
It was found that diaryldiazosulfides (I) reacted at an appreciable rate with β-naphthol in alkaline ethanol to produce azo-dyes. This is contrary to Hantzsch's observation. The initial-rate constants of the reaction were determined at various temperatures. The electron-donating substituents accelerated the rate when they were in the *N*-aryl part of I (substituent X) but retarded when in the *S*-aryl part of I (substituent Y). A set of ρ-values which have opposite signs, $\rho_X = -2.96$ and $\rho_Y = 3.93$, suggested that the rate-determining step in this reaction is the heterolytic rupture of the N–S bond of I. This was supported by the negative values of the entropy of activation and by such a solvent effect as that the rate was significantly increased when the polarity of the solvent increased. As the change in the concentration of β-naphthol affected the rate, the possibility of the participation of the transition state or of the intermediate including β-naphthol was also discussed.

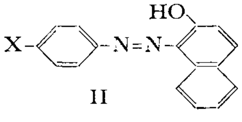
It has been known that the thermolysis of diaryldiazosulfides is available as a preparative route for the generation of aromatic thiyl radicals.[1)] Recently, Zwet and Kooyman[2)] also reported on kinetic studies of the homolysis of diazosulfides. However, few reports have been presented on the ionic reaction of diazosulfides. Hantzsch and Freese[3)] reported that diazosulfides dissociate to diazonium chloride and thiophenol in concentrated hydrochloric acid and that they do not give the coupling product with β-naphthol in alkaline ethanol.

We found that diaryldiazosulfides (I) reacted at an appreciable rate with β-naphthol in alkaline ethanol, thus producing azo-dyes (II).

In this paper, we wish to report our findings in a kinetic study of the reaction of diaryldiazosulfides with β-naphthol in alkaline ethanol.



I



II

Results and Discussion

Diaryldiazosulfides. The diaryldiazosulfides (I)

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[*2] Present address: Laboratory of Chemistry, Faculty of Science, Kōnan University, Okamoto, Higashinada-ku, Kobe.

[*3] Present address: Yokkaichi Division, Mitsubishi Petrochemical Co., Ltd., Toho-cho, Yokkaichi-shi, Mie.

1) a) E. C. Kooyman, "Organosulfur Chemistry," ed. by M. J. Janssen, Interscience Publishers, New York (1967), p. 9. b) W. B. Reynolds and E. W. Cotten, *Ind. Eng. Chem.*, **42**, 1905 (1950). c) S. Yamashita, J. Furukawa and T. Yamawaki, *Nippon Gomu Kyokaishi*, **31**, 534 (1958).

2) a) H. van Zwet and E. C. Kooyman, *Chem. Commun.* (London), **1965**, 313. b) H. van Zwet and E. C. Kooyman, *Rec. Trav. Chim. Pays-Bas*, **86**, 993 (1967). c) H. van Zwet and E. C. Kooyman, *ibid.*, **86**, 1143 (1967).

3) A. Hantzsch and H. Freese, *Ber.*, **28**, 3237 (1895).

TABLE 1. RATE CONSTANTS FOR THE REACTION OF DIAZOSULFIDES WITH β-NAPHTHOL IN ALKALINE ETHANOL AT VARIOUS TEMPERATURES*

	Substituent		$k\times10^5$ (sec^{-1})			
	X	Y	15.0°C	25.0°C	35.0°C	45.0°C
Ia	OCH_3	Cl	—	223	370	589
Ib	CH_3	Cl	65.3	122	207	353
Ic	H	Cl	23.0	53.8	122	248
Id	Cl	Cl	1.08	3.45	9.50	24.0
Ie	$COCH_3$	Cl	0.295	0.825	2.47	6.15
If	CN	Cl	—	0.0257	0.106	0.320
Ig	NO_2	Cl	—	—	0.0245	0.0717
Ih	Cl	OCH_3	—	0.0363	0.105	0.158
Ii	Cl	CH_3	0.0282	0.0945	0.278	0.752
Ij	Cl	H	0.107	0.320	1.03	2.62
Ik	Cl	$CONH_2$	4.37	13.9	36.2	87.2
Il	Cl	$COCH_3$	17.3	51.7	131	310
Im	Cl	CN	61.7	166	400	828

* [Diazosulfide]$=1.0\times10^{-4}$M, [β-Naphthol]$=1.0\times10^{-3}$M, [KOH]$=1.1\times10^{-3}$M

used in the present work all have their absorption maxima at 330—350 mμ (Table 6). According to the UV spectral discussion by Zwet and Kooyman,[2b)] all the diaryldiazosulfides (I) prepared in the present work may be assigned as the *trans* form. This assignment of their configuration is supported by such a phenomenon as the polymorphism; that is, the crystals of I prepared at a low temperature change in forms when left standing at room temperature (see Experimental Section). This change is probably to be ascribed to the isomerization from the *cis* form to the *trans*.

Reaction of Diaryldiazosulfides (I) with β-Naphthol in Alkaline Ethanol. Contrary to Hantzsch's observation,[3)] diazosulfides (I) reacted at an appreciable rate with β-naphthol in alkaline ethanol, thus producing azo-dyes (II). The products were identified by thin-layer chromatography (TLC).

The first-order rate plots of the reaction tended to curve more or less with the increase in the time (Fig. 1). This may be ascribed to the concurrent decomposition of I to diarylsulfides or disulfides,[2c)] the rates of which, in alkaline ethanol, are comparable to the rate of the reaction of I with β-naphthol,[4)] although the decomposition is overwhelmed by the coupling with β-naphthol and, accordingly, prevented fairly well in the presence of excess β-naphthol. Therefore, the initial-rate constants summarized in Table 1 will be utilized in the following discussion.

The electron-donating substituents accelerated the rate when they were in the N-aryl part of I, but retarded it when in the S-aryl part of I. A Hammett correlation of the rate constants at 35°C for diazosulfides (I) with substituents (Y) in the S-aryl part gives an excellent straight line, with a slope ρ_Y of 3.93 ($r=0.9997$) (Fig. 3), whereas a Hammett correlation for diazosulfides with substituents (X) in the N-aryl part shows a little poorer linearity, with a slope ρ_X of -3.92 ($r=0.979$). However, this latter linearity can be improved by eliminating the points for p-CN and p-NO_2 ($\rho_X=-2.96$, $r=0.985$) (Fig. 2). The deviation of these points below the line in Fig. 2 may be ascribed to an additional conjugation such as III and IV, which decreases the positive charge upon the diazonium part. Similar behavior was observed in the substituent effect on the rearrangement of N-methyldiaryltriazenes.[5)]

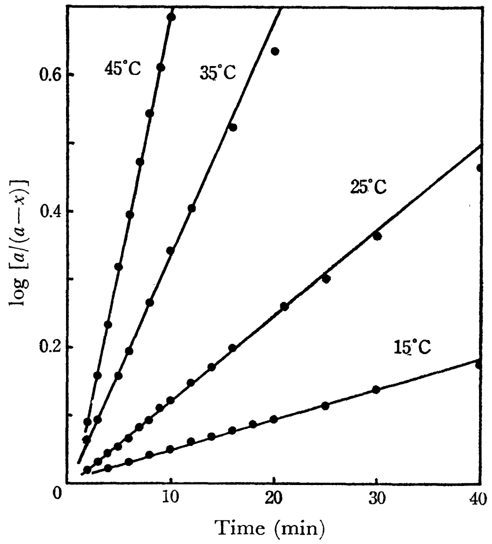


Fig. 1. First-order plots for the reaction of diazosulfide (Il) with β-naphthol in alkaline ethanol at various temperatures.

[4)] T. Yamada and N. Tanaka, unpublished work.

[5)] T. Yamada, This Bulletin, **42**, 3565 (1969).

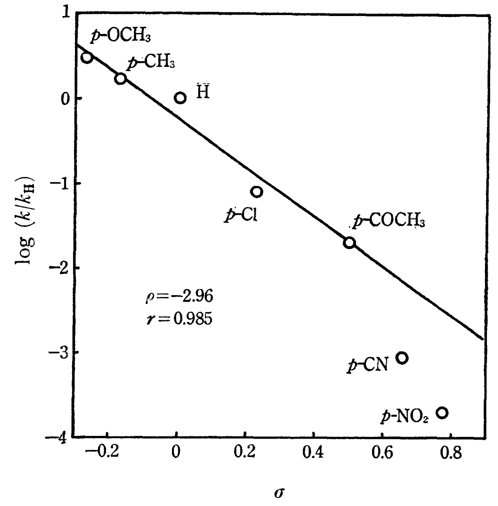


Fig. 2. Hammett plot for the reaction of diazosulfides (Ia—g), p-X-C_6H_4-N=N-S-C_6H_4-Cl-p, with β-naphthol in alkaline ethanol at 35.0°C.

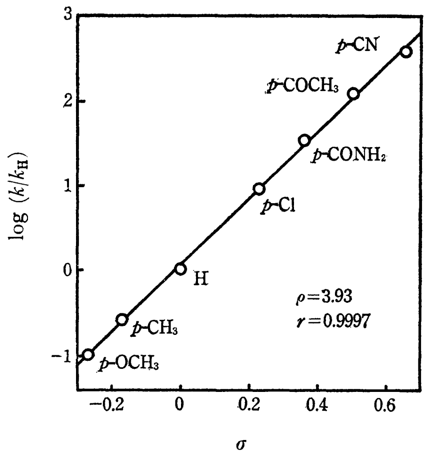
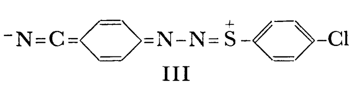
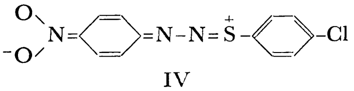


Fig. 3. Hammett plot for the reaction of diazosulfides (Ih—m, Id), p-Cl-C_6H_4-N=N-S-C_6H_4-Y-p, with β-naphthol in alkaline ethanol at 35.0°C.

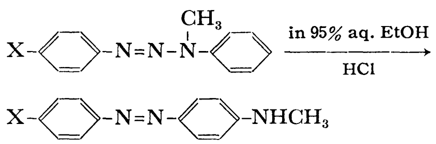


III



IV

A set of ρ-values which have opposite signs suggests that the heterolytic rupture of the N–S bond of diazosulfides (I) is the rate-determining step in this reaction, because a negative ρ_X-value and a positive ρ_Y-value suggest the stabilization of the diazonium cation by the substituents (X) in the N-aryl part and that of the thiophenoxide anion by the substituents (Y) in the S-aryl part. Similar substituent effects have been previously reported; for example, the following triazene rearrangement showed $\rho=-3.63$ (at 30.0°C).[5] The rate-determining step in the rearrangement was, therefore, concluded to be the dissociation of protonated triazene.



(1)

On the other hand, for the dissociation of m- and p-substituted thiophenols in 95% aqueous ethanol, $\rho=2.847$ (at 20—22°C) has been reported.[6] In this case, the use of σ^- rather than σ reduced the scatter in Hammett correlation. According to Tsuno,[7] the dissociation constants of m- and p-substituted thiophenols gave a good correlation with a value, 0.52, of the parameter, r, in the Yukawa-Tsuno equation. However, in the present reaction of I with substituents (Y) in the S-aryl part, a Hammett correlation using σ shows an excellent linearity ($r=0.9997$). Therefore, the contribution of the additional resonance stabilization by electron-withdrawing substituents seems to be less important in stabilizing the transition state in this reaction than in the case of the dissociation of thiophenols. This may be because the transition state of the reaction of I with β-naphthol may have a smaller charge separation than that of the dissociation of thiophenols.

TABLE 2. ACTIVATION PARAMETERS FOR THE REACTION OF DIAZOSULFIDES WITH β-NAPHTHOL IN ALKALINE ETHANOL

Diazosulfide	Substituent		E_a kcal/mol	$\Delta S^{\ddagger}$(35°C) e.u.
	X	Y		
Ia	OCH_3	Cl	9.1	−34.0
Ib	CH_3	Cl	10.3	−31.5
Ic	H	Cl	14.5	−18.0
Id	Cl	Cl	18.8	− 9.7
Ie	$COCH_3$	Cl	18.5	−13.7
Ii	Cl	CH_3	20.1	−12.3
Ij	Cl	H	20.0	−10.4
Ik	Cl	$CONH_2$	18.1	− 9.3
Il	Cl	$COCH_3$	17.5	− 8.9
Im	Cl	CN	15.7	−12.4

The thermodynamic parameters (Table 2) also suggest that the ionization of diazosulfides is rate-determining, because the values of E_a and $\Delta S^{\ddagger}$ fall within the range of the values found for a case in which the dissociation of neutral molecules to

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[6] H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

[7] Y. Tsuno, "Summary of the Symposium on the Hammett Relationship," the Chemical Society of Japan (1967), p. 4.

ions is rate-determining.[8] A plot of E_a against $\Delta S^{\neq}$ is found to show a linearity ($\beta \doteqdot 470°\text{K}$) (Fig. 4). The large negative values of $\Delta S^{\neq}$ for Ia and Ib may due to the substantial contribution of the entropy term to the reaction.

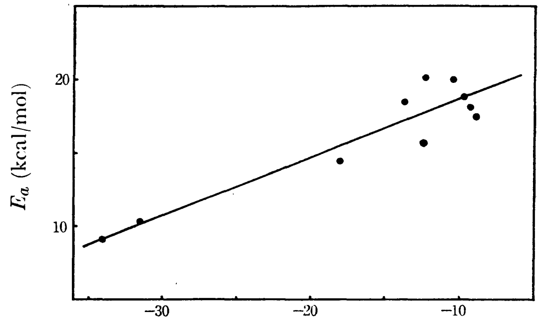


Fig. 4. Plot of E_a *vs.* $\Delta S^{\neq}$ for the reaction of diazosulfides with β-naphthol in alkaline ethanol.

According to Ingold's criterion,[9] this consideration can be supported by the findings concerning the solvent effect upon the rate constants; the rate significantly increased when the polarity of the solvent, ethanol, was increased by the addition of water (Table 3).

TABLE 3. EFFECT OF WATER CONCENTRATION ON THE REACTION CONSTANTS IN THE REACTION OF DIAZOSULFIDE (Id) WITH β-NAPHTHOL IN AQUEOUS ALKALINE ETHANOL AT 35.0°C*

H_2O (vol%)	$k \times 10^4$ (sec^{-1})
0	0.950
10	5.98
20	12.7
30	17.2
50*2	26.3

* [Diazosulfide] = 1.0×10^{-4}M, [β-Naphthol] = 1.0×10^{-3}M, [KOH] = 1.1×10^{-3}M

*2 [Diazosulfide] = 5.0×10^{-5}M, [β-Naphthol] = 5.0×10^{-4}M, [KOH] = 5.5×10^{-4}M

Table 4 shows that the increment in the concentration of KOH resulted in only a slight increase in the rate, while the addition of KCl also increased the rate in aqueous ethanol. These results can reasonably be interpreted in terms of the salt effect.

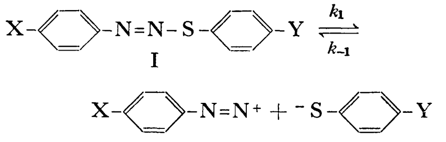
TABLE 4. EFFECT OF ALKALI CONCENTRATION ON THE RATE CONSTANTS IN THE REACTION OF DIAZOSULFIDES WITH β-NAPHTHOL AT 35.0°C

	[Diazosulfide] $\times 10^4$M	[β-Naphthol] $\times 10^4$M	[KOH] $\times 10^4$M	Solvent	$k \times 10^5$ sec^{-1}
Id	1.0	10	11	EtOH	9.50
Id	1.0	10	22	EtOH	10.0
Ic	1.0	10	11	EtOH	122
Ic	1.0	10	22	EtOH	136
Id	0.5	5.0	5.5	EtOH (50%) -H_2O (50%)	263
Id	0.5	5.0	0*	EtOH (50%) -H_2O (50%)*	243
Id	1.0	10	11*2	EtOH (50%) -H_2O (50%)	333

* Buffer solution (pH=9.4) was added.

*2 KCl was added (1.0×10^{-3}M).

From the available evidence, the most probable mechanism can be assumed to be as follows: diazosulfide dissociates to the diazonium cation and the thiophenoxide anion, and, then the former cation couples with the β-naphthoxide anion to produce azo-dye. The rate-determining step is the dissociation of diazosulfide; *i. e.*, $k_1 \ll k_2$, k_{-1}.



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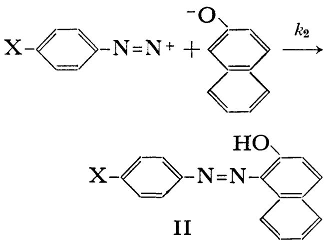
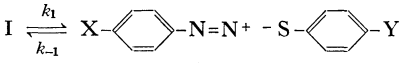


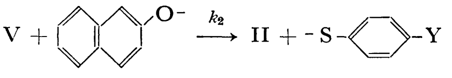
(3)

However, it is possible that the intermediate is an ion pair (V) rather than a free diazonium cation; that is, the ion pair intermediate (V) may be formed in the rate-determining step (Eq. (4)) and attacked by β-naphthol to produce II (Eq. (5)) ($k_1 \ll k_2$, k_{-1}).



(4)

V, ion pair



(5)

As is shown in Table 5, the change in the concentration of β-naphthol has an effect on the rate. The rate enhancement with the increase in β-naphthol is fairly large, but not so large that the order of reaction is one with respect to β-naphthol. Therefore, we may suggest the possibility of a

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[8] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., N. Y. (1961), p. 135.

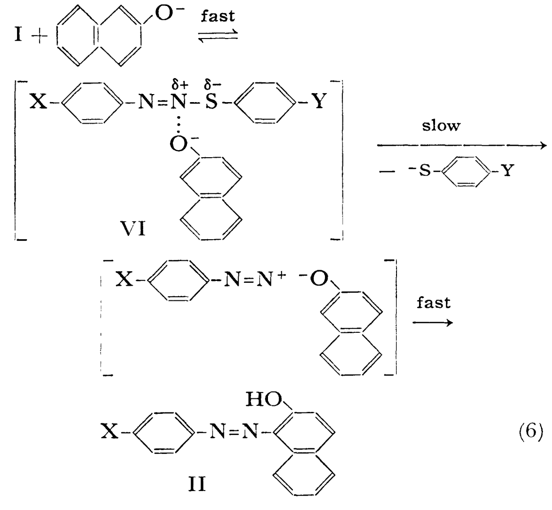
[9] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y. (1953), p. 345.

TABLE 5. EFFECT OF THE MOLAR RATIO OF β-NAPHTHOL TO DIAZOSULFIDE ON THE RATE CONSTANTS IN THE REACTION OF DIAZOSULFIDE (Id) WITH β-NAPHTHOL AT 35.0°C*

$\frac{[\beta\text{-Naphthol}]}{[\text{Diazosulfide}]}$	$k\times10^5$ (sec^{-1})		
	A	B	C
5	7.4	80.8	162
10	9.5	127	243
15	—	—	288
20	11.3	190	320

* [Diazosulfide] $=1.0\times10^{-4}$ M
A: solvent, EtOH; [KOH]/[β-Naphthol] = 1.1
B: solvent, 80% aq. EtOH, [KOH]/[β-Naphthol] = 1.1
C: solvent, EtOH (50%) + Buffer solution (pH 9.4) (50%)

"borderline" case[10] between S_N1 and S_N2; *i. e.*, in Eqs. (4) and (5), the rate of step 1 is comparable that of step 2. On the other hand, the possibility of an alternative mechanism through a loose "complex" (VI) containing β-naphthoxide cannot be disregarded (Eq. (6)).



However, the determination of the reaction order was difficult because the decomposition of I became predominant and made the rate plot complex in the presence of a low concentration of β-naphthol; thus, the role of β-naphthol in the rate enhancement is ambiguous.

On the basis of the above results, we consider the mechanism through the ion pair (Eqs. (4) and (5)) to be most likely in the reaction of I with β-naphthol. The rate enhancement with the increase in β-naphthol may be ascribed to the salt effect.

Zwet and Kooyman[2b] reported that the *cis* isomers react with β-naphthol in alkaline ethanol to form red azo-dye, whereas the *trans* isomers do not. Thus, they concluded that the ionization of diazosulfide could occur with only the *cis* isomers.

According to our present data on the substituent effect and the difference in the thiol acidities,[11] there is a considerable possibility that the following is true: the *trans*-diazosulfides studied by Zwet and Kooyman may also dissociate only very slowly, and this very slow dissociation seems to have led them to the mistaken conclusion that the *trans* isomer cannot undergo ionization. The same possibility may hold in the case of Hantzsch's report;[3] the diaryldiazosulfides used by Hantzsch and Freese may dissociate very slowly, judging from our results, and thus it seems that they failed to observe the reaction of diazosulfides with β-naphthol.

However, it becomes necessary to question whether or not the *trans* isomers dissociate through the *cis* forms. We intend to pursue this question through the isolation of *trans* and *cis* isomers of diazosulfides and by studying them kinetically in a subsequent paper.

Experimental

Preparation of Materials. *Most of the diaryldiazosulfides (I)* were synthesized by the following general method:[12]

A solution of 0.02 mol of *p*-substituted aniline in 20 m*l* of 7% hydrochloric acid was diazotized with 0.023 mol of sodium nitrite in 5 m*l* of water. The diazonium solution was then slowly added to an ice-cold, stirred solution of 0.02 mol of *p*-substituted thiophenol in 20 m*l* of a 10% aqueous sodium hydroxide solution. The yellow crystals which immediately formed were filtered, thoroughly washed with cold water, and dried *in vacuo* over calcium chloride. The crude products were dissolved in acetone at room temperature and recrystallized by cooling them in an acetone-dry ice refrigerant.

In the preparation of I, the following phenomena were observed. When the *S*-coupling was carried at 5—10°C, pale yellow crystals were first formed, but they soon rose to the surface of the liquid and became brownish. The brown solids were recrystallized from acetone to give pure yellow diazosulfide. On the other hand, when the *S*-coupling was carried below 0°C, the pale yellow crystals were obtained in a fairly stable form. However, they turned brownish upon filtration or desiccation at room temperature. Especially, when a large amount (0.1 mol) of Id was prepared, the yellow crystals turned exothermically into a brown mass, but a pure Id was obtained by several recrystallizations of the crude material. After recrystallization, no such change in I could be observed besides a gradual thermal decomposition.

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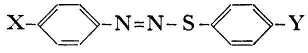
10) R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 362 (1969).

11) B. Dmuchovsky, F. B. Zienty and W. A. Vredenburgh, *J. Org. Chem.*, **31**, 865 (1966); the pK_a values at 27°C in 3 : 1 (*v*/*v*)-acetone-water are 11.1 for triphenylmethanethiol, 9.3 for 4-methylbenzenethiol, 8.6 for benzenethiol and 7.8 for 4-chlorobenzenethiol.

12) *Cf.* Refs. 1c, 2b and 3.

TABLE 6. THE ANALYTICAL DATA AND ULTRAVIOLET SPECTRAL DATA OF DIARYLDIAZOSULFIDES:



	Substituent X	Substituent Y	Mp °C	λ_{max} mμ	log ε	Analysis (calcd) C%	H%	N%
Ia	OCH_3	Cl	55.5—56.0	345	4.19	55.87 (56.01)	4.08 (3.98)	10.08 (10.05)
Ib	CH_3	Cl	66.0—66.5	336	4.13	59.24 (59.42)	4.19 (4.22)	10.75 (10.66)
Ic	H	Cl	34.0	332	4.06	57.70 (57.95)	3.63 (3.65)	11.36 (11.26)
Id	Cl	Cl	97.0—97.5	337	4.13	50.65 (50.90)	3.04 (2.85)	
Ie	$COCH_3$	Cl	80.5—81.0	342	4.17	58.13 (57.83)	3.79 (3.81)	9.64 (9.63)
If	CN	Cl	112.5—113.5	340	4.14	57.31 (57.04)	2.87 (2.95)	15.50 (15.35)
Ig	NO_2	Cl	111.5—112.0	350	4.16	48.92 (49.06)	2.57 (2.75)	14.43 (14.31)
Ih	Cl	OCH_3	59.0—59.5	333	4.11	56.27 (56.01)	4.00 (3.98)	10.00 (10.05)
Ii	Cl	CH_3	78.5—79.0	336	4.12	59.55 (59.42)	4.31 (4.22)	10.60 (10.66)
Ij	Cl	H	59.0—59.5	337	4.12	57.91 (57.95)	3.63 (3.65)	11.34 (11.26)
Ik	Cl	$CONH_2$	150	345	4.17	53.51 (53.53)	3.48 (3.46)	14.31 (14.41)
Il	Cl	$COCH_3$	104.5—105.5	349	4.22	57.68 (57.83)	3.84 (3.81)	9.82 (9.63)
Im	Cl	CN	109.0—109.5	346	4.22	56.84 (57.04)	2.88 (2.95)	

Diazosulfides (Im and Ik) were prepared as follow: *p*-aminobenzonitrile (5.9 g) was treated by the usual procedure[13] to convert an amino group to a mercapto group, but in order to avoid the hydrolysis of a cyano group, the hydrolysis of the intermediate, *p*-cyanophenyl ethyl xanthate, was carried out by standing overnight at room temperature. Nevertheless, a mixture of *p*-cyanothiophenol and *p*-carbamoylthiophenol was obtained. From this mixture, a mixture (9 g) of diazosulfides, Im and Ik, was obtained by the procedure described above. The mixture was added to benzene (90 m*l*), stirred well at room temperature, and filtered from the insoluble material. To filtrate, after the benzene was distilled off *in vacuo*, was purified by elution chromatography over the activated alumina, using benzene as the eluent. The compound that was first eluted, the predominant component, was identified as diazosulfide (Im) on the basis o the elementary analysis and a study of the infrared spectrum (ν_{CN}=2270 cm^{-1}). The yield of Im was 6 g. On the other hand, the insoluble material (1.2 g) was recrystallized from acetone and gave diazosulfide (Ik) ($\nu_{C=O}$=1693 cm^{-1}, ν_{NH_2}=3480, 3590 cm^{-1}). The analytical data and the ultraviolet spectral data of I are summarized in Table 6.

α-(p-Substituted phenylazo)-β-naphthols (II) were prepared by the reaction of the corresponding aryldiazonium chlorides and β-naphthol in an aqueous alkaline solution by the usual procedure, and were purified by several recrystallizations from ethanol (Table 7). The λ_{max} and ε values for II, summarized in Table 7, were measured, under conditions similar to those holding in the reaction of diazosulfides with β-naphthol, as follows: an ethanol solution (1 m*l*) of II (10^{-3}M), 1 m*l* of a 1.1×10^{-2}M KOH ethanol solution, and 0.9 m*l* of $1.0\times$

TABLE 7. PHYSICAL CONSTANTS AND ULTRAVIOLET SPECTRAL DATA* OF α-ARYLAZO-β-NAPHTHOLS (II)

Substituent X	Mp °C	λ_{max} mμ	ε
OCH_3	136—137	458	15000
CH_3	132.5—134	476	13400
H	133—134	476	14300
Cl	165—166	476	15900
Cl	165—166	486^{*2}	19000^{*2}
$COCH_3$	186—187	485	22800
CN	239—240	480	20400
NO_2	251—252	494	20600

* Solvent: EtOH

^{*2} Solvent: EtOH (50%) - water (50%)

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[13] D. S. Tarbell and D. K. Fukushima, "Organic Syntheses," Coll. Vol. III, p. 809 (1955).

10^{-2}M β-naphthol ethanol soultion were placed in a 10-m*l* measuring flask, and then, by the subsequent addition of ethanol, the solution was made up to volume. This solution was used as the sample for the visible spectra measurements.

Kinetic Measurements. The rate constants were determined spectrophotometrically. A Hitachi Perkin-Elmer 139 UV-VIS spectrophotometer equipped with a thermostated cell compartment was used.

One m*l* of a β-naphthol ethanol solution (10^{-2}M), 1 m*l* of a KOH ethanol solution (1.1×10^{-2}M), and about 6.5 m*l* of ethanol were placed in a 10-m*l* measuring flask immersed in a thermostated water bath. The reaction was initiated by the addition of 1 m*l* of an ethanol solution of diazosulfide (10^{-3}M), freshly prepared at the same temperature, to the flask. The entire solution was then quickly made up to volume with ethanol, and the solution was transferred into a 10-mm stoppered quartz cuvette set in a thermostated cell compartment.

The optical densities were measured at appropriate intervals at the maximum-absorption wavelength of the azo-dye produced.

In the present work, it was assumed that the amount of azo-dye produced (x) was equal to that of diazosulfide consumed; thus, the rate constants were evaluated from the slope of the plot of log ($a/(a-x)$) against t, where a is the initial concentration of diazosulfide. A typical example is shown in Fig. 1. In most of the reactions, the rate decreased with time, and so the initial rates were measured (Table 1).

On the reaction in a mixture of ethanol and a buffer solution, Clark-Lubs's buffer solution (pH 9.4) was used, and the initial concentrations of I and β-naphthol were half as much as those in the general procedure described above because of the low solubility of the azo-dye produced in this solvent.

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