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Studies of Diazosulfides. II.*[1] The Dissociation of *trans*- and *cis*-Diazosulfides and the Isolation of *cis*-Diaryldiazosulfides

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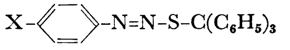
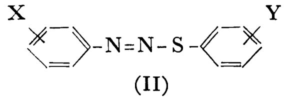
The reaction of *trans*- and *cis*-*N*-aryl-*S*-triphenylmethyldiazosulfides (I) with *β*-naphthol in alkaline ethanol was investigated. It was found that the dissociation of I occurs not only with the *cis* isomers, but also with the *trans* isomers, even in the dark. The kinetic study suggested that the *trans*-diazosulfides can dissociate not only through the *cis* form, but also directly, contrary to Zwet and Kooyman's suggestion. The dissociation of the *trans* isomer of diaryldiazosulfides (II) was also discussed analogously. Further, by a preparation at −78°C several *cis*-diaryldiazosulfides were isolated which had never before been isolated. The rate constant of the isomerization of *cis*-*N*-(*p*-cyanophenyl)-*S*-(*p*-tolyl)diazosulfide (IIf) was 2.55×10^{-3} sec^{-1} (at 0°C, in ethanol); this value is much larger than that for *cis*-I.

Recently, both *cis* and *trans* isomers of diazosulfides were isolated by Zwet and Kooyman.1) In their paper, it was concluded that the ionization of diazosulfides can occur with only the *cis* isomers, whereas the *trans* isomer cannot dissociate unless it is first converted photochemically to the *cis* isomer. Similar behavior has been reported for diazocyanides and diazosulfonates.2) However, the present author and his co-workers found previously that diaryldiazosulfides, which could be identified as having the *trans* form according to the UV spectral discussion,1) dissociated at an appreciable rate and coupled with *β*-naphthol to afford azo-dyes in alkaline ethanol.3) On the basis of the previous results,3) it was suggested that the *trans* form of diazosulfides may generally dissociate, and that the *trans*-*N*-aryl-*S*-triphenylmethyldiazosulfides (I) treated by Zwet and Kooyman also dissociate, even though at a very low rate. In other to confirm this suggestion, the present author prepared both *trans* and *cis* forms of I and examined their reaction with *β*-naphthol. Further, in connection with the study of the dissociation of *trans*-diaryldiazosulfides (II), the author could successfully isolate the *cis* isomers of II, which had never before been isolated.

In the present paper, the author wishes to report the findings of his kinetic study of the reaction of *cis* and *trans* forms of diazosulfides (I) with *β*-naphthol in alkaline ethanol, and of his study of the isolation of *cis*-II isomers and their thermal isomerization.



(I)



(II)

Results and Discussion

Reaction of *cis*- and *trans*-Diazosulfides (I) with *β*-Naphthol. The reaction of *trans*-*N*-aryl-*S*-triphenylmethyldiazosulfides (I) with *β*-naphthol was carried out in alkaline ethanol at 30.0°C. It was found that the *trans*-diazosulfides (Ia–c, X= OCH_3, CH_3 and H) reacted very slowly, but positively, to produce azo-dyes even in the dark, contrary to Zwet and Kooyman's observation.1)

TABLE 1. RATE CONSTANTS FOR THE REACTION OF *N*-ARYL-*S*-TRIPHENYLMETHYL DIAZOSULFIDES (I) WITH *β*-NAPHTHOL IN ALKALINE ETHANOL*

		$k\times10^6$ (sec^{-1})		
	Substituent	*cis*-I	*trans*-I	
	X	35.0°C	35.0°C	45.0°C
Ia	OCH_3		1.9	6.5
Ib	CH_3	140	0.49	1.8
Ic	H	65	0.096	0.38
Id	Cl	16	—**	—**
Ie	NO_2	1.6	—**	—**

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

** too slow to measure.

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*[1] Part I of this series: Ref. 3.

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1) H. van Zwet and E. C. Kooyman, *Rec. Trav. Chim. Pays-Bas*, **86**, 993 (1967).

2) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York (1961), pp. 66, 151.

3) T. Yamada, N. Tanaka, T. Morisawa, M. Nishikuri and A. Kaji, This Bulletin, **43**, 908 (1970).

The first-order rate constants of the reaction of *cis*-and *trans*-I are summarized in Table 1. The table shows that the *cis* isomer reacts much faster than the *trans* isomer, as is expected, and that the electron-donating substituents on the *N*-aryl part of both *cis*-I and *trans*-I promote the reaction. Hammett plots of the rate constants give good straight lines, the ρ-values being -2.05 for the *cis* isomers (ρ_{cis}) and -4.8 for the *trans* isomers (ρ_{trans}) (Fig. 1).

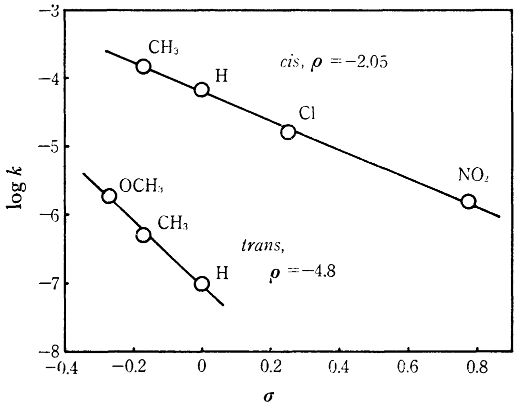


Fig. 1. Hammett plots for the reaction of *cis*- and *trans*-diazosulfides (I), p-X-C_6H_4-N=N-S-$C(C_6H_5)_3$, with β-naphthol in alkaline ethanol at 35.0°C.

Table 2. Activation parameters for the reaction of *trans*-diazosulfides (I) with β-naphthol in alkaline ethanol

Diazosulfide	Substituent X	E_a kcal/mol	$\Delta S^{\neq}$ (35°C) e. u.
Ia	OCH_3	24.0	−10.2
Ib	CH_3	25.4	−8.4
Ic	H	26.8	−7.2

Table 2 summarizes the activation parameters calculated from the values for the *trans* isomers listed Table 1. It is interesting that the values of the entropy of activation ($\Delta S^{\neq}$) are comparable with the values for diaryldiazosulfides, whereas the energies of activation (E_a) were considerably larger than that for diaryldiazosulfides; *e.g.*, the E_a value for *N*-(*p*-tolyl)-*S*-(*p*-chlorophenyl)diazosulfide is 10.2 kcal/mol.[3]

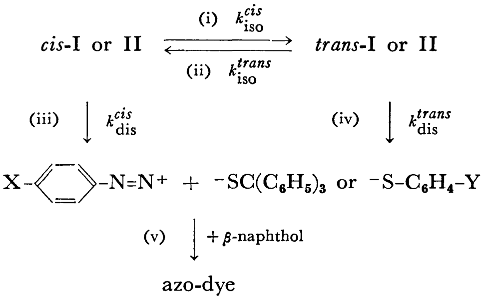
The negative ρ-values (Fig. 1) and the negative values of the entropy of activation (Table 2) suggest that the rate-determining step in this reaction is the dissociation of diazosulfides (I), just as in the case of diaryldiazosulfides (II).[3] Therefore, it seems reasonable that the following discussion of the dissociation of diazosulfides is based on the rate constants shown in Table 1.

The rate constants of the reaction of *cis*-I with β-naphthol at 30.0°C in alkaline ethanol are 10^{-4}—10^{-6} sec^{-1} (Table 1), whereas the isomerization rate constants of *cis*-I at 36.9°C in chloroform are 5×10^{-4}—7×10^{-4} sec^{-1}.[1] Therefore, even if the small solvent effect on the isomerization rate[1] is taken into account, it seems that the thermal *cis*→*trans* isomerization does not proceed through ionization and recombination, as Zwet and Kooyman suggested.

The present author observed the dissociation of the *trans*-diazosulfides. It is also a question whether this dissociation proceeds through the *cis* isomer analogously to Zwet and Kooyman's conclusion (Mechanism A), or whether it occurs directly from the *trans* isomer (Mechanism B). However, Mechanism A will be excluded by the following discussion.

The reaction was always carried out in the dark, and the solution of diazosulfides was quickly prepared in a room lighted as usual. No rate change was observed even for the solution prepared in the dark. Therefore, the photochemical *trans*→*cis* isomerization can be disregarded. We must, then, assume that the *trans*→*cis* isomerization occurs thermally in the course of the reaction of the *trans*-I with β-naphthol if the reaction proceeds by means of Mechanism A.

As has been described above, the rate-determining step of this reaction should be the dissociation of diazosulfides. Table 1 shows that the reaction of the *cis* isomer is much faster than that of the *trans* isomer. Therefore, even if the reaction of the *trans* isomer proceeds *via* the *cis* form, Step (iii) in Scheme 1 cannot be rate-determining.



Scheme 1

On the other hand, Zwet and Kooyman showed that the substituent effect for the *cis*→*trans* isomerization (Step (i)) is negligible. Therefore, on the basis of the principle of the microscopic reversibility, it seems valid to say that the substituent effect on Step (ii) is negligible. This is not, however, in accord with the observed result ($\rho_{trans}=-4.8$). Therefore, it seems unreasonable to say that Step (ii) is the rate-determining step in the reaction of *trans*-I with β-naphthol.

Consequently, it seems reasonable to conclude that the *trans*-diazosulfides (I) dissociate directly, not through the *cis* forms. This may explain well the finding that ρ_{trans} is not the same as ρ_{cis}.

Although the rate data for the dissociation of the *cis* isomers are lacking, the same mechanism may hold for the dissociation of the *trans*-diaryldiazosulfides (II) described in a previous paper ;[3] if *trans*-II cannot dissociate directly, *i.e.*, if $k_{\rm dis}^{trans} \doteqdot 0$, then $k_{\rm dis}^{cis} \ll k_{\rm iso}^{trans}$ would be valid because the rate-determining step is the heterolytic rupture of the N–S bond of diazosulfide.[3] We shall suppose that the thermal equilibirum between the *cis* form and the *trans* is attained and that its equilibrium constant, $K(=k_{\rm iso}^{cis}/k_{\rm iso}^{trans})$ is larger than 10^2.[4] On the other hand, the isomerization rate constant for *cis*-IIf at 35°C ($k_{\rm iso}^{cis}$), is estimated, by extrapolation from the data shown in Table 4, to be *ca.* 10^{-1} sec^{-1}. This figure gives $k_{\rm iso}^{trans} \leqq 10^{-3}$ sec^{-1} (35°C) ; thus, $k_{\rm dis}^{cis} \ll 10^{-3}$ sec^{-1}. If the substituent effect on the isomerization is neglected as in the case of diazosulfides (I), the rate constant for the net reaction, $k(=k_{\rm dis}^{cis}/K)$, can be expected to be much smaller than 10^{-5} sec^{-1}. The actually-observed rate constants, however, are 4×10^{-3}—10^{-6} sec^{-1} (35°C). Therefore, the *trans* isomers of diaryldiazosulfides also seem to dissociate not through the *cis* form, but directly. In Scheme 1, Steps (iii) and (iv) are shown to be irreversible, because Step (v) may be much faster than those steps.

Isolation of *cis*-Diaryldiazosulfides (IV). Hantzsch and Freese[5] speculated that, in the preparation of diaryldiazosulfides, the *cis* form is first produced, but that it is immediately isomerized to the *trans* form. Similar examples have been reported for diazocyanides and diazosulfonates.[2]

As the bulky mercaptans (*e.g.*, triphenylmethylmercaptan and *t*-butylmercaptan) seemed, on the basis of Zwet and Kooyman's results, to prevent the *cis*→*trans* isomerization, the author first used 2,6-dimethylthiophenol to prepare diaryldiazosulfides (II) at −10——5°C. However, they were all assigned to the *trans* isomer on the basis of the UV spectra, *i.e.*, $\lambda_{\rm max}$ (Table 5) and the lack of spectral change. The Hammett plot of the rate constants for the reaction of II with β-naphthol in alkaline ethanol, summarized in Table 3, shows a straight line with a value of $\rho=-5.2$ (Fig. 2) ; this value is comparable with the value for the same reaction of the *trans*-I. It is interesting that the point for IIa falls on the line when the σ-value for the 2,6-dimethyl group is assumed to be equal to twice $\sigma_{p\text{-CH}_3}$ In other words, the steric effect by two *ortho*-methyl groups of mercaptan does not operate in this instance.

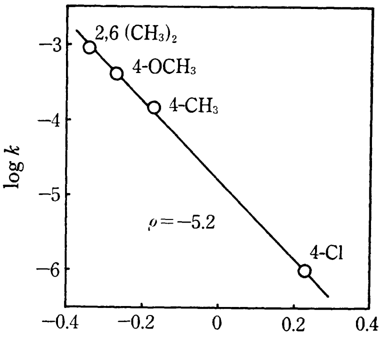


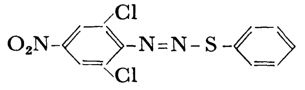
Fig. 2. Hammett plot for the reaction of diazosulfides (IIa-d), X-C_6H_4-N=N-S-$C_6H_3(CH_3)_2$-(2,6), with β-naphthol in alkaline ethanol at 35.0°C.

TABLE 3. RATE CONSTANTS FOR THE REACTION OF *N*-ARYL-*S*-(2,6-DIMETHYLPHENYL)DIAZOSULFIDES (II) WITH β-NAPHTHOL IN ALKALINE ETHANOL AT 35.0°C*

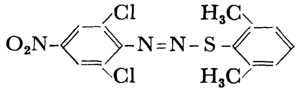
	Substituent X	$k\times10^4$ sec^{-1}
IIa	2,6-$(CH_3)_2$	8.5
IIb	4-OCH_3	4.0
IIc	4-CH_3	1.5
IId	4-Cl	0.010

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

Further, the diazosulfides (IV and V), which have substituents in two *ortho*-positions of the *N*-aryl part, were also prepared. Although they do not have a $\lambda_{\rm max}$ beyond 320 mμ, they also seem to be *trans* isomers because no spectral change was observed at room temperature. The substituents in the *ortho*-positions of the *N*-aryl part, even in the *trans* form, seem to make it difficult for the aromatic ring to be coplanar to the plane containing the N=N group.



IV, $\lambda_{\rm max}^{\rm EtOH}$ 320 mμ (317 mμ)[6]



V, $\lambda_{\rm max}^{\rm EtOH}$ 315 mμ

Next, diazosulfides were prepared at −78°C. In this case, the diazonium salts with an electron-withdrawing substituent and the mercaptans with an electron-donating substituent were employed so that the *S*-coupling would proceed quickly, even at a low temperature. As a result, the *cis* isomers of five diaryldiazosulfides were isolated, as is shown in Figs. 3 and 4. Figure 5 shows the spectra of the *cis* isomers. These spectral changes cannot be ascribed to the transformations of the ionic dia-

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4) This assumption seems to be valid because the *cis* isomer could not be detected in the recrystallized *trans* isomer.

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

6) C. C. Price and S. Tsunawaki, *J. Org. Chem.*, **28**, 1867 (1963).

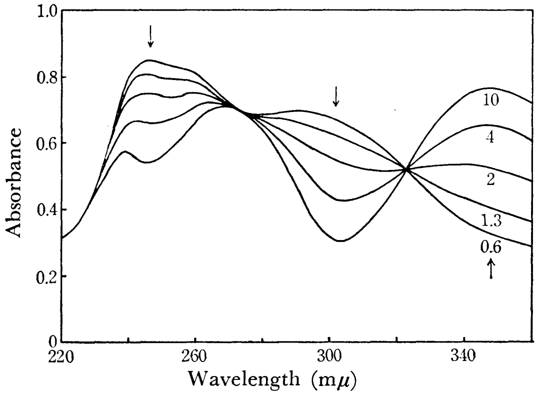

Fig. 3. The progressive spectral change in the *cis*→*trans* isomerization of *cis*-diazosulfide, *p*-O_2N-C_6H_4-N=N-S-C_6H_4-CH_3-(*p*), in ethanol. Numbers refer to time after sample was dissolved (in minutes).

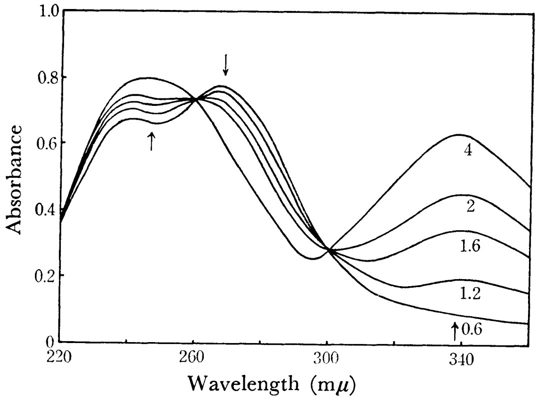

Fig. 4. The progressive spectral change in the *cis*→*trans* isomerization of *cis*-diazosulfide, *p*-NC-C_6H_4-N=N-S-C_6H_4-CH_3-(*p*), in ethanol. Numbers refer to time after sample was dissolved (in minutes).

zonium thiophenoxides into the covalent diazosulfides because of the following evidence: (i) The spectra shown in Fig. 5 have $\lambda_{\max}$ values different from those for the diazonium ions. (ii) *p*-cyanobenzenediazonium ion instantaneusly reacted with *β*-naphthol in alkaline ethanol to afford red azo-dye at −78°C, whereas diazosulfide (IIf), which was prepared at the same temperature and which was identified as a *cis* isomer, did not react under the same conditions.

The diazosulfides (IV and V) were also prepared at −78°C, but the products were still *trans* isomers. Accordingly, *ortho*-substituents seem to hinder the formation of the *cis* isomer or make the *cis*→*trans* isomerization occur more rapidly.

The rate constants of the thermal isomerization of *cis*-IIf were determined in ethanol (Table 4). It is noteworthy that the entropy of activation is fairly small compared with that for the *cis*-Ic ($\Delta S^{\ddagger}=18.6$ e.u.). The energy of activation for *cis*-IIf is comparable to other examples of the *cis*→*trans* isomerization (*e.g.*, Ic: 29.2 kcal/mol,[1] azonaphthalene: 22.0kcal/mol,[7] azobenzene: 23.0 kcal/mol,[8] diazocyanide: 21.5 kcal/mol,[9] and diazosulfonate: 14.7 kcal/mol[10]).

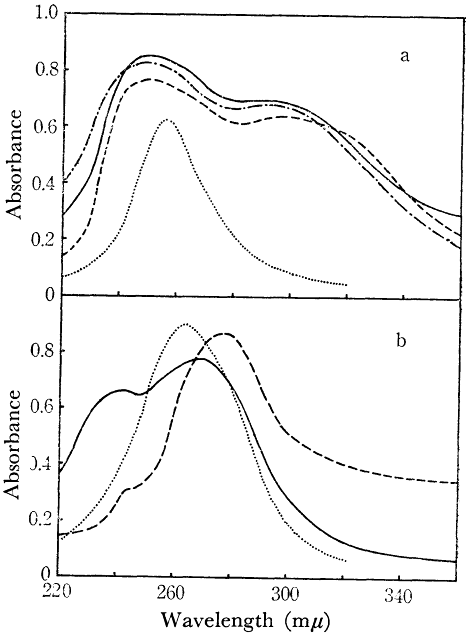

Fig. 5. Absorption spectra of *cis*-diaryldiazosulfides and diazonium ions in ethanol. a) *p*-O_2N-C_6H_4-N=N-S-Ar; ——: Ar=*p*-tolyl, —·—·: Ar=*p*-chlorophenyl, ----: Ar=2,6-dimethylphenyl. ······: *p*-O_2N-C_6H_4-$N_2^+\cdot HSO_4^-$ b) *p*-NC-C_6H_4-N=N-S-Ar; ——: Ar=*p*-tolyl, ----: Ar=2,6-dimethylphenyl. ······: *p*-NC-C_6H_4-$N_2^+\cdot Cl^-$.

TABLE 4. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE ISOMERIZATION OF *cis*-*N*-(*p*-CYANOPHENYL)-*S*-(*p*-TOLYL)DIAZOSULFIDE(IIf) IN ETHANOL

Temp. (°C)	$k\times10^4$ (sec^{-1})	
−20	1.28	E_a=20.5 kcal/mol
−10	6.08	$\Delta S^{\ddagger}$=2.9 e. u.
0	25.5	

Experimental

Preparation of Materials. All the *cis*- and *trans*-*N*-aryl-*S*-triphenylmethyldiazosulfides (I) were prepared

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7) M. Frankel, R. Wolovsky and E. Fisher, *J. Chem. Soc.*, **1955**, 3441.

8) G. S. Hartley, *ibid.*, **1938**, 638.

9) R. J. W. Le Fèvre and H. Vine, *idib.*, **1938**, 431.

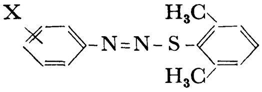
10) E. S. Lewis and H. Suhr, *Chem. Ber.*, **92**, 3031 (1959).

TABLE 5. THE PHYSICAL CONSTANTS AND ULTRAVIOLET SPECTRAL DATA OF DIAZOSULFIDES (I)

	Substituent X	*cis*-I		*trans*-I	
		mp (°C)	λ_{max} (mμ)*	mp (°C)	λ_{max} (mμ)*
Ia	OCH_3			112(dec.)	343
Ib	CH_3	88	318	117(dec.)	338
Ic	H	94	312	122(dec.)	335
Id	Cl	96	317	130(dec.)	340
Ie	NO_2	95	304	145(dec.)	359

* in benzene

TABLE 6. THE ANALYTICAL DATA AND ULTRAVIOLET SPECTRAL DATA OF DIAZOSULFIDES (II):



	Substituent X	Color	mp °C	λ_{max}^{EtOH} mμ	Analysis (calcd)		
					C%	H%	N%
IIa	2,6-$(CH_3)_2$	Yellow	52	310*			
IIb	*p*-OCH_3	Yellow	67	345			
IIc	*p*-CH_3	Yellow	70	330	70.58 (70.28)	6.12 (6.29)	10.78 (10.93)
IId	*p*-Cl	Yellow	95	332	60.46 (60.75)	4.85 (4.73)	9.84 (10.12)
IIe	*p*-CN	Yellow	109—110	334	67.14 (67.39)	4.70 (4.90)	15.42 (15.72)
IIg	*p*-NO_2	Orange	75— 76	345	56.92 (57.14)	3.81 (4.06)	15.27 (15.38)

* shoulder

by the method of Zwet and Kooyman.[1] The physical constants and the UV spectral data of the I thus prepared are summarized in Table 6. The *trans*-*N*-aryl-*S*-(2,6-dimethylphenyl)diazosulfides (IIa–e, g) were prepared by the method described in a previous paper.[3] The analytical data, physical constants, and UV spectral data of II are summarized in Table 5. The α-(2,6-dimethylphenylazo)-β-naphthol was prepared by a method described previously.[3] Mp 147°C, λ_{max} 484 mμ ε 14300 (in alkaline ethanol).

Found: C, 78.44; H, 5.67; N, 10.16%. Calcd for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14%.

The UV spectral data of the other azo-dyes were reported in the previous paper.[3]

Kinetic Measurements. The rate constants for the reaction of diazosulfides (I and II) with β-naphthol in alkaline ethanol were determined spectrophotometrically, as has been described previously.[3] The order of reaction with respect to β-naphthol could not be determined.[3] Accordingly, the rate was measured in the presence of excess β-naphthol. In most of the reactions, a rate depression with the time was observed; this may be ascribed to the competitive isomerization or decomposition of diazosulfides. Thus, the initial rates were measured; they are summarized in Tables 1 and 3.

Isolation of *cis*-Diaryldiazosulfides. The *cis*-diaryldiazosulfides were prepared as follows: a solution of 2 mmol of *p*-nitroaniline in 4 m*l* of 10% hydrochloric acid was diazotized with 2mmol of sodium nitrite in 1 m*l* of water at −5——10°C. The diazonium solution was then added to a stirred solution of 2 mmol of *p*-methylhiophenol in 50 m*l* of alkaline ethanol, while the mixture was being cooled by an acetone-dry ice bath. Yellow crystals of *cis*-diazosulfide were immediately formed. The yellow crystals were collected on a well-cooled filter, washed with cold ethanol (*ca.* −70°C), and preserved at

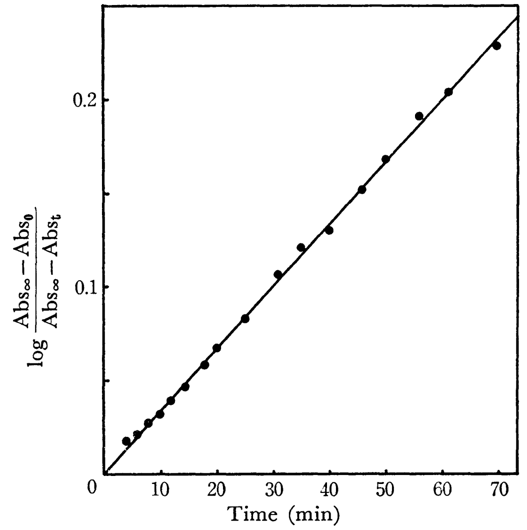


Fig. 6. First-order rate plot for the isomerization of *cis* isomer of diazosulfide (IIf), *p*-NC-C_6H_4-N=N-S-C_6H_4-CH_3-(*p*), in ethanol at −20.0°C.

about −70°C. At this temperature, no change was observed in the UV spectra for at least a day.

Isomerization of *cis*-Diaryldiazosulfides. The isomerization was followed spectrophotometrically using a Hitachi rapid scan spectrophotometer. Some of the *cis*-diazosulfide was dissolved in cold ethanol in a flask immersed in an acetone-dry ice bath. The solution was then quickly transferred into a well-cooled quartz cuvette set in the cell holder, and immediately the UV spectrum was recorded by an oscilloscope unit at appropriate intervals. Because an ambient temperature cell compartment was used, the solution in a cuvette rapidly warmed up, and then the isomerization proceeded acceleratively. Some examples of the spectral change with the time are shown in Figs. 3 and 4.

Kinetic Measurements of the Isomerization of *cis*-*N*-(*p*-Cyanophenyl)-*S*-(*p*-tolyl)diazosulfide (IIf). The rate constants of the isomerization of *cis*-IIf were determined spectrophotometrically. An appropriate amount of *cis*-IIf was dissolved in ethanol so that the concentration of the solution became suitable for the spectral measurements. The temperature was kept constant in a salt-ice bath using a thermos.

Aliquots were removed at intervals and put into a quartz cuvette set in a cell compartment, and the optical densities were immediately measured at 340 mμ (see Fig. 4), the absorption maximum of *trans*-IIf. The first-order rate constants were evaluated by the graphical method shown in Fig. 6 and are summarized in Table 4.

A solution of *cis*-IIf in ethanol can be stored without change for at least two hours at −78°C.

The author wishes to thank Professor Ryōzō Gotō for his encouragement of this work. He is also indebted to Professors Aritsune Kaji and Jun-ichi Hayami for their valuable discussions, and to Mr. Masao Nishikuri for his earnest assistance.