BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2032—2035(1972)

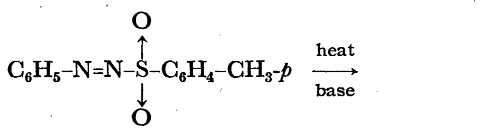
Kinetic Study on Homolysis of Aryl Arylazo Sulfones[1]

Minoru KOJIMA, Hiroshi MINATO, and Michio KOBAYASHI*
Department of Chemistry, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo

(Received December 7, 1971)

Aryl arylazo sulfones were prepared, and the rates of homolyses in chlorobenzene were determined in the presence of a base for suppression of acid catalysis at 80—118°C. An isokinetic relationship was found to hold between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ ($\beta=101.0$°C). The substituents on the benzenesulfonyl group influenced the rates very little, whereas the substituents on the phenylazo group decreased the rates (especially the electron-releasing substituents).

Phenylazo *p*-tolyl sulfone was found to undergo homolysis when such bases as pyridine, quinoline, and magnesium oxide were present for suppression of heterolysis catalyzed by acidic products.[2)]



$$C_6H_5\text{-}N{=}N\text{-}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}\text{-}C_6H_4\text{-}CH_3\text{-}p \xrightarrow[\text{base}]{\text{heat}} C_6H_5\cdot + N_2 + \cdot O_2S\text{-}C_6H_4\text{-}CH_3\text{-}p$$

Rates of homolyses of substituted phenylazotriphenylmethanes[3)] and aryl arylazo sulfides[4)] were reported. In contrast to the case of substituted benzoyl peroxides, the rates of decomposition of these azo compounds containing electron-releasing and electron-withdrawing substituents (except that with *p*-methyl) were smaller than that of the non-substituted azo compounds. The effect of the substituents of aryl arylazo sulfones on the rates of decomposition appears to be of great interest, and kinetic studies have been carried out in chlorobenzene. The results will be described in the present paper.

---

* To whom correspondence should be sent.

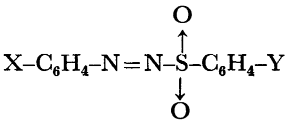
1) Organic Sulfur Compounds, Part XXVIII.

2) M. Kobayashi, H. Minato, M. Kojima, and N. Kamigata, This Bulletin, **44**, 2501, (1971).

3) T. Yamamoto, *Nippon Kagaku Zasshi*, **83**, 844, (1962).

4) H. van Zwet and E. C. Kooyman, *Rec. Trav. Chim. Pays-Bas*, **86**, 1143, (1967).

Table 1. Physical properties of aryl arylazo sulfones



$$X\text{-}C_6H_4\text{-}N{=}N\text{-}\overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{S}}}\text{-}C_6H_4\text{-}Y$$

	Substituents		Mp (°C) (decomp.)	Color	Elemental analysis (%)				Ref.
					Found		Calcd		
	X	Y			C	H	C	H	
a	p-$(CH_3)_2N$	p-CH_3	130—131	reddish purple	59.45	5.91	59.40	5.65	
b	p-CH_3O	p-CH_3	110—111	yellow	58.20	4.60	57.92	4.86	(9)
c	p-CH_3	p-CH_3	96— 97	orange					(7)
d	p-Cl	p-CH_3	118—119	yellow					(7)
e	p-NO_2	p-CH_3	135—136	orange	51.03	3.42	51.14	3.63	
f	m-CH_3O	p-CH_3	84— 85	yellow	58.06	4.66	57.92	4.86	
g	m-CH_3	p-CH_3	69— 70	yellow					(7)
h	m-NO_2	p-CH_3	113—114	yellow	51.21	3.70	51.14	3.63	
i	H	p-CH_3	90— 91	yellow					(7)
j	H	H	76— 77	orange					(8)
k	H	p-Cl	94— 95	yellow	51.13	3.30	51.33	3.23	
l	H	m-NO_2	89— 90	yellow	49.38	3.03	49.48	3.11	

Experimental

Materials. Aryl arylazo sulfones except the p-dimethylamino derivative were prepared from substituted benzenediazonium chlorides and sodium salts of substituted benzenesulfinic acids according to the method of Hantzsch.[5]

p-Dimethylaminophenylazo p-tolyl sulfone was prepared by isolating p-dimethylaminobenzenediazonium fluoroborate[6] and letting it react with sodium p-toluenesulfinate in water.

Kinetic Measurements. Since the thermal homolyses of aryl arylazo sulfones are complicated because of the occurrence of the heterolyses catalysed by the acidic products (sulfonic acids, sulfinic acids),[2] the rates of decomposition were determined in the presence of pyridine (3 mol per mol of an azosulfone) except the p-dimethylamino azosulfone. The rates of decomposition of p-dimethylaminophenylazo p-tolyl sulfone were determined in the presence of triethylamine (3 mol per mol of the azosulfone), since the azosulfone itself possesses a basicity comparable to that of pyridine.

An azosulfone (3 mmol) was dissolved in a mixture of chlorobenzene (60 m*l*) and pyridine (or triethylamine) in a flask placed in a constant-temperature bath. Decomposition was followed by determining the amount of nitrogen gas evolved by use of a gas buret. The evolution of nitrogen was almost quantitative (more than 90%) with all the azosulfones.

Results and Discussion

Aryl arylazo sulfones prepared are summarized in Table 1. The rates of decomposition of these azosulfones followed first-order equations when a base was present. Some examples are shown in Fig. 1. From the rate constants at four or five different temperatures, activation parameters were obtained. Tables 2 and 3 show the rate constants and activation parameters. Figure 2 shows that an isokinetic relationship holds

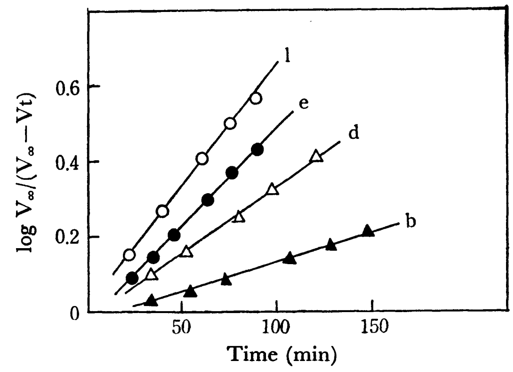


Fig. 1. Typical plots for the rates of decomposition of aryl arylazo sulfones in chlorobenzene at 90.6°C. (Letters in the figure correspond to the compounds described in Table 1. V_∞ and V_t are the volumes of the nitrogen evolved at time ∞ and time t, respectively.)

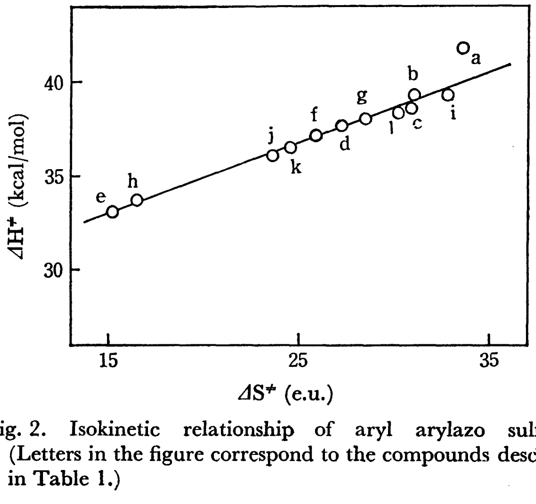


Fig. 2. Isokinetic relationship of aryl arylazo sulfones. (Letters in the figure correspond to the compounds described in Table 1.)

---

5) A. Hantzsch and M. Singer, *Ber.*, **30**, 312 (1897), **31**, 636, (1898).

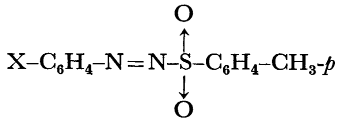
6) G. Shiemann and W. Winkelmuller, *ibid.*, **66**, 727, (1933).

7) P. K. Dutt, H. R. Whitehead, and A. Wormall, *J. Chem. Soc.*, **119**, 2088, (1921); *ibid.*, **125**, 1463, (1924).

8) C. G. Overberger and A. J. Rosenthal, *J. Amer. Chem. Soc.*, **82**, 108, (1960).

9) R. L. Schlessinger, U. S. 2588885 (1952).

TABLE 2. RESULTS OF DECOMPOSITION OF SUBSTITUTED PHENYLAZO p-TOLYL SULFONES IN CHLOROBENZENE

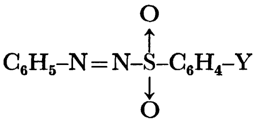


$$X\text{-}C_6H_4\text{-}N{=}N\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}C_6H_4\text{-}CH_3\text{-}p$$

Substituents		$10^4\times k(\text{sec}^{-1})$[a]						$\Delta H^{\neq}$	$\Delta S^{\neq}$
	X	80.0°C	85.4°C	90.6°C	95.6°C	99.4°C	102.7°C	(kcal/mol)	(e.u.)
b	p-CH$_3$O			0.697	1.38	2.24	4.21	39.4	30.0
c	p-CH$_3$		0.638	1.41	2.85	4.07		38.7	29.9
d	p-Cl		0.696	1.39	2.09	5.06		37.7	27.2
e	p-NO$_2$		1.16	2.08	4.06	6.81		33.1	15.2
f	m-CH$_3$O		0.797	1.51	2.84	6.13		37.1	25.9
g	m-CH$_3$		0.961	1.66	3.45	6.72	10.8	38.1	28.5
h	m-NO$_2$		0.897	1.58	3.12	5.48		33.7	16.5
i	H	0.494	1.08	2.52	5.38			39.4	32.8
				$10^4\times k(\text{sec}^{-1})$					
			105.0°C	109.0°C	115.0°C		118.0°C		
a	p-(CH$_3$)$_2$N		1.13	2.17	5.36		7.23	41.8	33.5

a) Rate constants are reproducible within ± 3%.

TABLE 3. RESULTS OF DECOMPOSITION OF ARYL PHENYLAZO SULFONES IN CHLOROBENZENE



$$C_6H_5\text{-}N{=}N\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}C_6H_4\text{-}Y$$

Substituents		$10^4\times k$ (sec^{-1})						$\Delta H^{\neq}$	$\Delta S^{\neq}$
	Y	80.0°C	85.4°C	90.6°C	95.6°C	99.4°C	102.7°C	(kcal/mol)	(e.u.)
j	H	0.536	1.16	2.68	4.63			36.0	23.5
i	p-CH$_3$	0.494	1.08	2.52	5.38			39.4	32.8
k	p-Cl			2.07	4.14	6.93	10.86	36.5	24.5
l	m-NO$_2$		1.35	2.46	4.73	9.38		38.4	30.2

between the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values, and β is equal to 101.0°C. This fact suggests that all the azosulfones decompose by the same mechanism.

Figure 3 is the plots of log k_X/k_H *versus* the Hammett σ values for substituted phenylazo p-tolyl sulfones at 90.6°C. It is remarkable that the rates of all the substituted azosulfones are smaller than that of phenylazo p-tolyl sulfone itself, and the rates of the azosulfones with electron-releasing substituents are especially small. A

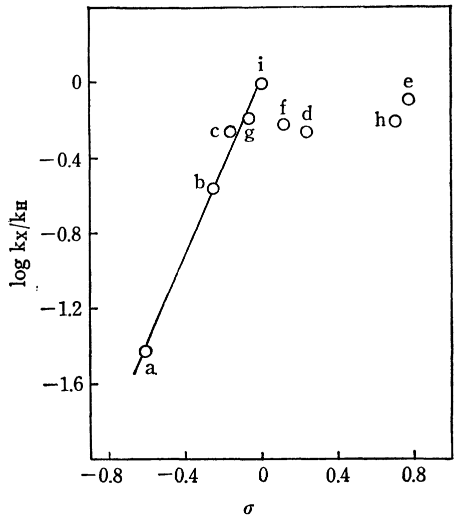


Fig. 3. Relationship between σ values and log k_X/k_H (90.6°C) (Letters in the figure correpond to the compounds described in Table 1. The value for a was calculated from those at higher temperatures.)

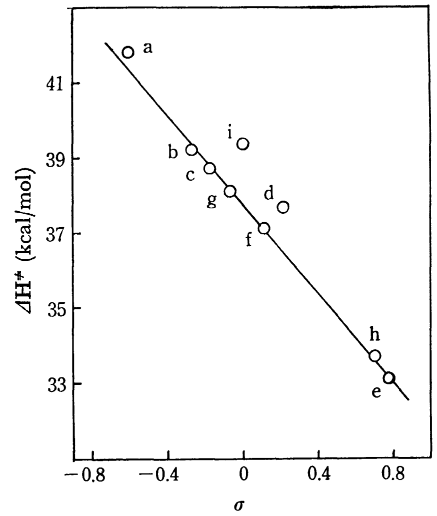


Fig. 4. Relationship between $\Delta H^{\neq}$ and σ values. (Letters in the figure correspond to the compounds described in Table 1.)

linear relationship seems to hold for azosulfones containing electron-releasing substituents, but not for those with electron-withdrawing substituents. These findings are in contrast with the results with substituted phenylazotriphenylmethanes and aryl arylazo sulfides; in the latter cases, the rates of the azo compounds containing electron-withdrawing substituents were especially small.

Figure 4 shows that a fair linear relationship holds between $\Delta H^{\neq}$ and the Hammett σ values.

The $\Delta S^{\neq}$ values for these azosulfones are much greater than those of other azo compounds. It is likely that in the ground states, these azosulfones are greatly polarized and strongly solvated, whereas in their transition states the C–N and S–N bonds are stretched and the extent of solvation is much smaller, and therefore the $\Delta S^{\neq}$ values are very large.

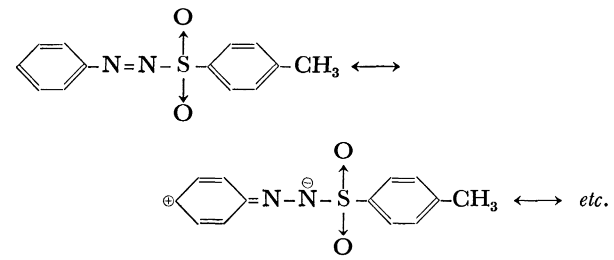
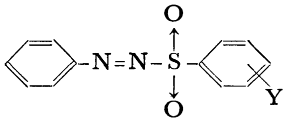
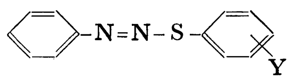


Table 3 summarizes the rate constants of aryl phenylazo sulfones. The rate constants do not vary greatly with the substituents. These results are in contrast with those of p-MeC_6H_4–N=N–S–C_6H_4–Y (for example, $k_H/k_{p\text{-}NO_2}$ is equal to about 20).[4]





It is reasonable that the strength of the N–S bond of the azosulfide is greatly influenced by the resonance involving the S lone pair and the electrophilic substituents on the benzene ring, whereas the strength of the N–S bond of the azosulfone is very little affected by the substituents across the sulfonyl group.

Aryl arylazo sulfones can be synthesized very easily and are fairly stable (no decomposition for several months at 0°C). Therefore, they are very useful as a source of substituted phenyl free radicals.