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CIDNP Studies of the Thermal Decomposition of Arylazo Aryl Sulfones

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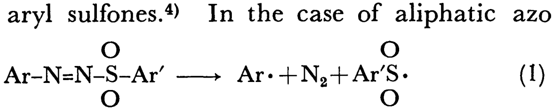
^{1}H-and ^{13}C-CIDNP spectra were obtained during the thermal decomposition of several arylazo aryl sulfones (Ar–N=N–SO$_2$–Ar′) in tetrachloroethylene or 1,1,2,2-tetrachloroethane at 100 °C. An enhanced absorption from the C$_1$ of the starting material, azo sulfone, was observed; this indicates that the decomposition of azo sulfone proceeds by means of one-bond fission. The formation of sulfones (ArSO$_2$Ar′) and sulfinic esters (ArO(SO)Ar′) as recombination products in a solvent cage was established from the signs of polarization (enhanced absorption or emission).

Arylazo aryl sulfones (**1**) decompose unimolecularly when they are heated in neutral or weakly basic media;[1] the generation of an aryl and sulfonyl radical pair has been proposed on the basis of kinetics,[2] product studies,[3] or the spin trapping of free radicals generated from the arylazo aryl sulfones.[4] In the case of aliphatic azo

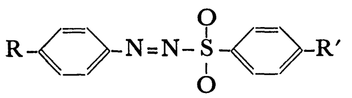


$$\text{Ar–N=N–}\overset{\text{O}}{\underset{\text{O}}{\text{S}}}\text{–Ar}' \longrightarrow \text{Ar}\cdot + \text{N}_2 + \text{Ar}'\overset{\text{O}}{\underset{\text{O}}{\text{S}}}\cdot \qquad (1)$$

compounds such as α,α′-azobisisobutyronitrile, solvent-cage products of the geminate radical pair are the main products. On the other hand, the homolysis of arylazo aryl sulfones gives the expected cage product, sulfones (ArSO$_2$Ar′), in only a small yield. These sulfones may be either cage-recombination products or products of the induced decomposition of the azo sulfones by aryl radicals. We have, therefore, studied the ^{1}H-and ^{13}C-CIDNP spectra (chemically induced dynamic nuclear polarization) observed during the thermolysis of several arylazo aryl sulfones in order to clarify the details of the reaction mechanism; the results will be presented in this paper.

Results and Discussion

The thermal decomposition of arylazo aryl sulfones (**1a**—**g**) was carried out in tetrachloroethylene or 1,1,2,2-tetrachloroethane.



	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1a**-d_3
R	H	Me	Cl	NO$_2$	NMe$_2$	H	H	D(2,6-D$_2$)
R′	Me	Me	Me	Me	Me	H	Cl	Me

Decomposition of Azo Sulfones in Tetrachloroethylene. The rate of the decomposition of **1a** in tetrachloroethylene was determined by following the evolution of the nitrogen gas by the method described in Ref. 2. The reaction was first-order in **1a**, and the rate constant was calculated to be 6.10×10^{-4} s^{-1} (90.8 °C). This value is comparable to those in ethylbenzene, chlorobenzene, or nitrobenzene.[2] The decomposition products of **1a** are shown in Table 1.

When the ^{1}H-NMR spectra of **1a**—**d** and **1f**—**g** were observed at 100 °C, strong CIDNP signals appeared in the field of the aromatic-proton region for about 15 min. No CIDNP signal was, though, observed in the field of the methyl-proton region. Since **1e** is rather stable and decomposes very slowly at 100 °C,[1] no CIDNP signal could be observed. To prevent the acid-catalyzed heterolysis of **1**, the ^{1}H-NMR spectra were observed in the presence of 2 mol of triethylamine per mol of azo sulfones. The CIDNP spectrum of **1a** under these conditions is shown in Fig. 1. Enhanced absorption signals were observed in the field of δ 7.89—7.72 and 7.10, and strong emission signals were observed at δ 7.30 and 7.20. The intensity of the CIDNP

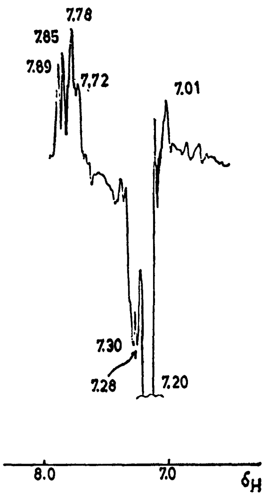


Fig. 1. ^{1}H-CIDNP spectrum in the thermal decomposition of **1a** in the presence of triethylamine in tetrachloroethylene at 100 °C.

Table 1. Products of thermal decomposition of **1a** in tetrachloroethylene

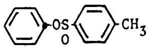
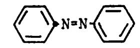
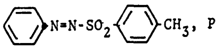
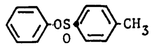
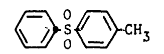
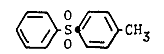
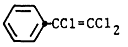
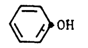
Product	Yield/mol%	Product	Yield/mol%
PhCCl=CCl$_2$	21.9	p-CH$_3$C$_6$H$_4$SO$_2$Cl	16.9
PhCl	6.1	p-CH$_3$C$_6$H$_4$SO$_2$Ph	6.5
PhH	4.9	p-CH$_3$C$_6$H$_4$SO$_2$OPh	27.7
Ph-N=N-Ph	3.5	p-CH$_3$C$_6$H$_4$SO$_2$SC$_6$H$_4$CH$_3$-p	14.1
		p-CH$_3$C$_6$H$_4$SO$_3$H	*ca.* 20

signal at δ 7.20 was very high when triethylamine was added. The ^{1}H-NMR spectrum of 2,4,6-trideuteriophenylazo *p*-tolyl sulfone (**1a**-d_3) at 100 °C was also observed. The enhanced absorption at δ 7.89—7.72 and the emission of δ 7.30 observed in **1a** disappeared, while an enhanced absorption appeared at δ 7.31. The strong emission at δ 7.20 was still observed with **1a**-d_3. From the results described above, and by comparison with the chemical shift of the authentic samples, some signals were assigned as is shown below:

Enhanced absorption	at δ 7.89—7.72	*o*-H of the phenyl group of phenyl p-tolyl sulfone(**2a**)
Emission	at δ 7.30	*o*-H of α,β,β-trichlorostyrene
Emission	at δ 7.20	Benzene

The assignment of the ^{13}C-CIDNP signals can be expected to be easier than that of the ^{1}H-CIDNP signals, so the ^{13}C-NMR spectrum of **1a** at 100 °C was observed. CIDNP signals were also obtained in the field of the aromatic region for more than 20 min. The intensity of the CIDNP signals as a whole increased when pyridine was added to prevent acid-catalyzed heterolysis. The observed CIDNP spectrum of **1a** in the presence of pyridine is shown in Fig. 2, while the chemical shifts and assignments of the CIDNP signals are tabulated in Table 2. The signals were assigned by comparison with the chemical shifts of the authentic samples of the products, shown in Table 2.

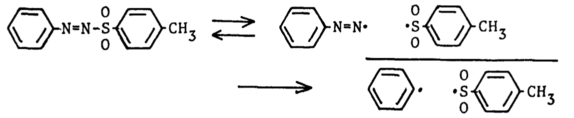
TABLE 2. ^{13}C-CIDNP DATA FOR THERMAL DECOMPOSITIN OF **1a**[a)]

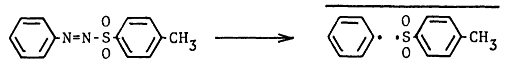
No.[b)]	Chemical shift[c)]	Polarization	Assignment[d)]
1	153.2	A	
2	152.3	E	
3	149.2	A	, Pyridine
4	142.6	E	
5	142.3	A	
6	139.1	E	
7	136.7	E	Not assigned
8	135.0	E	
9	134.6		Pyridine
10	122.5		Pyridine
11	119.7		Solvent
12	157.7	A	

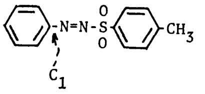
a) Pulse interval, 3 s; accumulation, 20; spectral width, 2.5 KHz; data memory, 4K, and pulse width, 9 μs (45° pulse). b) Signal number shown in Fig. 2. c) Ppm from internal TMS. d) • shows polarized carbons.

On the basis of the CIDNP data, the following conclusions could be drawn:

1) As has been mentioned before, azo sulfones decompose unimolecularly. Mechanistically, there may be two possible decomposition modes: one is the one-bond fission to give an aryldiazenyl sulfonyl radical pair (Eq. 2), while the other is the two-bond fission to give an aryl radical, a sulfonyl radical, and nitrogen simultaneously (Eq. 3). The observation of the enhanced absorption of the C_1 of **1a** itself indicates that the decomposition of **1a** is reversible, and so it must take place by means of one-bond fission. The sign in the net polarization (Γ_{ne}), as calculated according to Kaptein's rule[5)] agrees with the observed mode:


(2)

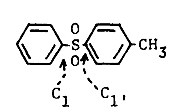

(3)



	μ	ε	Δg	a	Γ_{ne}	obsd
C_1	−	+	−	+[6)]	+	A

$g<2.0010$[7)] (Ph–N=N•); 2.0041[8)] ($\cdot SO_2C_6H_4CH_3$-*p*)

2) If one assumes that the sulfone (**2a**) obtained from the decomposition of **1a** is the cage product, the sign in the net polarization (Γ_{ne}), as calculated according to Kaptein's rule, again agrees with the observed mode:

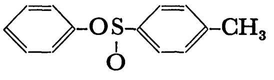


	μ	ε	Δg	a	Γ_{ne}	obsd
C_1	−	+	−	+[9)]	+	A
$C_{1'}$	−	+	+	+[10)]	−	E

$g=2.00234$[11)] (Ph•)

The observation of the CIDNP signals of sulfone (**2a**) and the coincidence of the signs mentioned above indicate that **2a** is the cage product from the phenyl *p*-toluenesulfonyl singlet-radical pair.

3) As is shown in Table 1, phenyl *p*-toluenesulfinate (**3a**) was not detected among the decomposition products of **1a**. In the ^{13}C-CIDNP spectra of **1a** shown in Fig. 2, however, the emission and enhanced absorption signals of this sulfinic ester (**3a**) were observed for 2.5—3.5 min. Also, the sign of the net polarization (Γ_{ne}), as calculated according to Kaptein's rule, agrees with the observed results if one assumes that **3a** is the cage product:



	μ	ε	Δg	a	Γ_{ne}	obsd
C_1	−	+	−	+	+	A
$C_{1'}$	−	+	+	+	−	E

Since **3a** is unstable,[12)] it could not be isolated as a product of the decomposition of **1a**. The ^{13}C-CIDNP study described here shows that not only the sulfone (**2a**), but also the sulfinic ester (**3a**) is generated as the

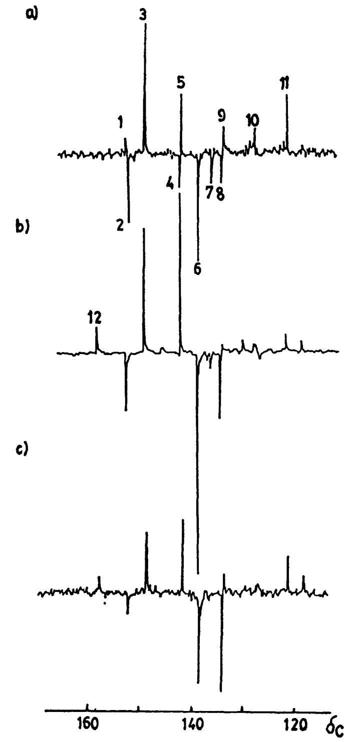
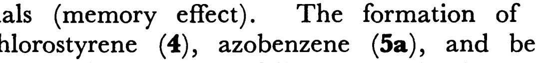
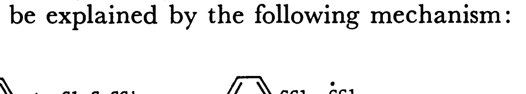


Fig. 2. ^{13}C-CIDNP spectra in the thermal decomposition of **1a** in the presence of pyridine in tetrachloroethylene.
After a) 2.5—3.5, b) 8—9, and c) 20—21 min heating of **1a** in NMR probe at 100 °C.

cage product from the phenyl *p*-toluenesulfonyl radical



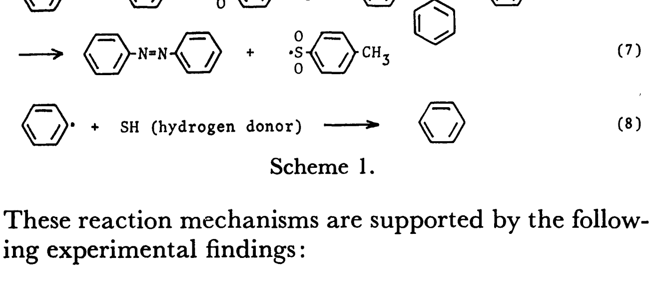
(4)



(5)

pair. These findings clearly establish that the sulfonyl radical is ambident and acts as either an S- or O-centered radical.

Scavenged products of the escaped phenyl radical in which polarization is maintained should show emission signals (memory effect). The formation of α,β,β-trichlorostyrene (**4**), azobenzene (**5a**), and benzene can be explained by the following mechanism:



Scheme 1.

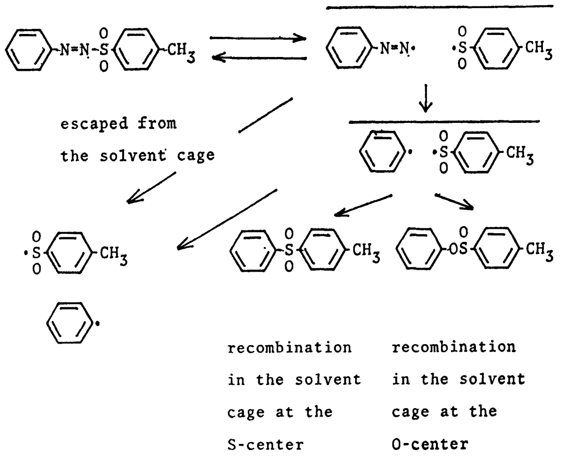
These reaction mechanisms are supported by the following experimental findings:

(i) When a large amount of the azo sulfone (**1a**) was present at the beginning of the decomposition, the intensity of the CIDNP signal of azobenzene (**5a**) was very strong, but toward the end of the reaction it decreased. On the other hand, the intensity of the CIDNP of α,β,β-trichlorostyrene (**4**) increased toward the end of the reaction.

(ii) When the ^{13}C-NMR spectrum of a mixture of **1a** and **1c** was measured at 100 °C, the CIDNP signal of 4-chloroazobenzene (4-ClC_6H_4–N=N–Ph **5b**) also appeared. This shows that the escaped phenyl radical attacks both **1a** and **1c**. As has been mentioned before, the rate of the decomposition of **1a** was first-order in **1a**, but a high concentration of azo sulfone at the beginning of the decomposition may favor the induced decomposition (Eq. 7).

(iii) The intensity of the emission of the benzene proton (δ 7.20) was strengthened in the presence of triethylamine. This shows that the escaped phenyl radical abstracts hydrogen from the *N*-ethyl group in the presence of triethylamine.

In conclusion, ^{1}H-and ^{13}C-CIDNP studies support the idea that the thermal decomposition of **1a** in a solvent cage occurred according to Scheme 2 and that the reaction mechanism of the escaped phenyl radicals is explained by Scheme 1.



Scheme 2.

Decomposition of Azo Sulfones in 1,1,2,2-Tetrachloroethane. The decomposition of azo sulfone in 1,1,2,2-tetrachloroethane, which may act as a hydrogen donor, was also studied. The rate of the decomposition of **1a** at 90.1 °C was determined by measuring the amount of nitrogen gas by the method described in Ref. 2. It followed a first-order rate equation in **1a** at the beginning of the reaction and they increased toward the end of the reaction. This may be explained by the acid-catalyzed ionic decomposition due to the formation of sulfinic or sulfonic acid. The decomposition products of **1a**, as summarized in Table 3, show that the products and their yields in 1,1,2,2-tetrachloroethane were different from those in tetrachloroethylene.

When the ^{1}H-NMR of **1a** was measured in 1,1,2,2-tetrachloroethane at 100 °C, a strong emission signal was observed at δ 7.29, just as in tetrachloroethylene.

TABLE 3. PRODUCTS OF THERMAL DECOMPOSITION OF **1a** IN 1,1,2,2-TETRACHLOROETHANE

Product	Yield/mol%	Product	Yield/mol%
PhH	36.0	$PhSO_2C_6H_4CH_3$-*p*	8.1
PhCl	14.8	*p*-$CH_3C_6H_4SO_2Cl$	9.6
Cl_2C=CHCl	17.3	*p*-$CH_3C_6H_4SO_2OPh$	18.5
Ph-N=N-Ph	1.3	*p*-$CH_3C_6H_4SO_2SC_6H_4CH_3$-*p*	12.6
		p-$CH_3C_6H_4SO_3H$	*ca.* 20

In the presence of 2 mol of triethylamine per mol of azo sulfone, the intensity of the emission signal at δ 7.29 increased, but not so markedly as in the case of tetrachloroethylene. These CIDNP signals were assigned to benzene. The escaped phenyl radical mainly abstracts hydrogen from the solvent, since the solvent is the hydrogen donor.

Experimental

The ^{1}H-NMR spectra were taken with a Hitachi R-20B spectrometer. The ^{13}C-NMR spectra were taken with a JEOL Fx-60 FT-NMR spectrometer.

Materials. All the arylazo aryl sulfones except **1e** were prepared from the substituted benzenediazonium chlorides and sodium salts of the substituted benzenesulfinic acid.[1] Compound **1e** was prepared from *p*-dimethylaminobenzenediazonium tetrafluoroborate and sodium *p*-toluenesulfinate in water.

Products of Thermal Decomposition of 1a. After the decomposition was complete, the reaction mixture was washed with a 5% aqueous solution of sodium carbonate. The benzene, chlorobenzene, and trichloroethylene were then determined by gas chromatography. The other products listed in Table 1 or 3 were separated by column chromatography on Florisil. Each product was identified by means of its mp, IR, and ^{1}H-NMR spectra. The sodium carbonate extracts were concentrated under reduced pressures and made weakly acidic by the addition of hydrochloric acid, and the *p*-toluenesulfonic acid in the solution was precipitated as its *S*-benzylisothiuronium salt.

CIDNP Spectra. A solution of azo sulfone (*ca.* 0.2 mol/l) in tetrachloroethylene or 1,1,2,2-tetrachloroethane was inserted in a NMR probe which had been heated at 100 °C, and the ^{1}H-NMR or ^{13}C-NMR was measured.

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