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Photolysis of Phenylazo *p*-Tolyl Sulfones[1]

Michio KOBAYASHI, Sadao FUJII, and Hiroshi MINATO
Department of Chemistry, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo

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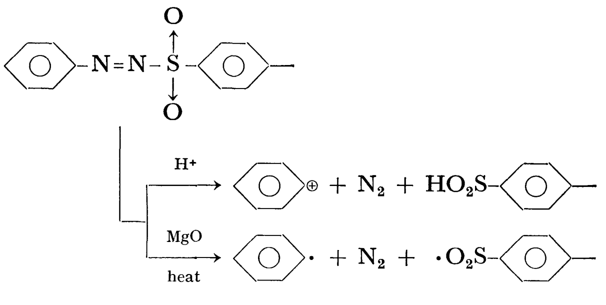
Photolysis of phenylazo *p*-tolyl sulfone and *p*-chlorophenylazo *p*′-tolyl sulfone in aromatic solvents at room temperature was investigated. The products were analyzed, and the isomer distribution and partial rate factors in arylation of mono-substituted benzenes were determined. The results indicate that the photolysis involves formation of aryl radicals and *p*-tolylsulfonyl radicals.

Arylazo aryl sulfones are interesting compounds; they undergo both heterolysis and homolysis. As an example, when phenylazo *p*-tolyl sulfone (I) is placed in an acidic medium, phenyl cation is formed,[2] whereas I yields phenyl radical when it is heated in a medium containing magnesium oxide, pyridine, or quinoline which captures *p*-toluene sulfonic acid.[3]

Thermal decomposition of I in a non-acidic medium is not so fast, and the half-life at 60°C is about 20 hr



($\Delta H^{\neq}=30.8$ kcal/mol, $\Delta S^{\neq}=10.7$ e.u./mol)[3] in ethylbenzene.

Since azosulfones absorb at wavelength over 400 nm owing to the *n*-π^* transition of the azo group, they are

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[1] Organic Sulfur Compounds. Part XXXII.

[2] M. Kobayashi, H. Minato, and N. Kobori, This Bulletin, **43**, 219 (1970).

[3] M. Kobayashi, H. Minato, M. Kojima, and N. Kobori, *ibid.*, **44**, 2501 (1971).

expected to undergo photolysis. The photolyses of I and *p*-chlorophenylazo *p*'-tolyl sulfone (II) have been investigated in aromatic solvents, and the results are described in this paper.

Results and Discussion

Solutions of I in equimolar mixtures of benzene and a monosubstituted benzene were degassed and irradiated with a high pressure mercury lamp at room temperature. Considerable amounts of biaryls were isolated when reaction mixtures were washed with water and the organic layers were subjected to column chromatographic separation on Florisil or alumina. Quantitative determination of biphenyl and substituted biphenyl isomers were carried out by gas chromatography, and the partial rate factors were calculated. As regards anisole or nitrobenzene, photolysis was performed in a mixture with chlorobenzene instead of benzene, and the amounts of substituted biphenyls formed were determined. The partial rate factors in these solvents were calculated by using the partial rate factors in chlorobenzene. The results are summarized in Table 1.

Table 1. Isomer distributions and partial rate factors in phenylation with I

Substrate	Isomer distribution (%)			Partial rate factors		
	o	*m*	*p*	*o*	*m*	*p*
Anisole	72.6	13.5	13.9	4.99	0.94	1.92
Ethylbenzene	54.8	29.6	15.6	2.41	1.30	1.37
Chlorobenzene	62.5	22.5	15.0	2.95	1.06	1.42
Benzonitrile	50.0	20.0	30.0	3.64	1.46	4.37
Nitrobenzene	61.7	13.2	25.1	5.34	1.14	4.37

When the values of log (partial rate factors at para positions) were plotted *versus* the Hammett σ-values, a V-shaped line was obtained as shown in Fig. 1. The ρ value for the right half was +0.90 (γ, 0.988), which is comparable to the ρ value (1.21) obtained by the thermal homolysis of I.[3] The isomer distributions and partial rate factors shown in Table 1 are similar to those obtained with phenyl radical (Table 2 (a)), but quite different from those with phenyl cation (Table 2 (b)).[2]

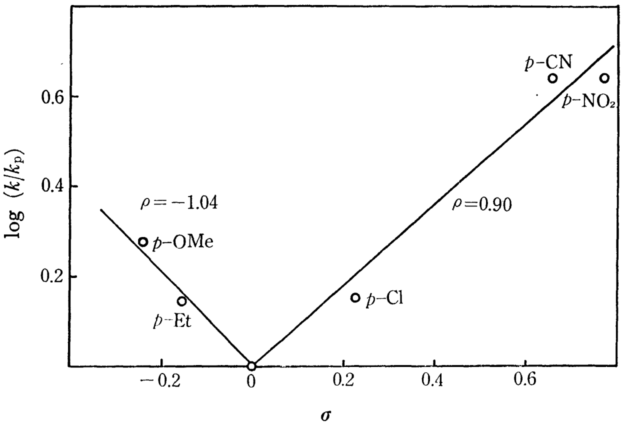


Fig. 1. The Hammett plots for phenylation of substituted benzenes by phenylazo *p*-tolyl sulfone

These data indicate that the biphenyls shown in Table 1 arose from the attack of phenyl radical on aromatic solvents. The free-radical nature of the substitution is exemplified by the values in benzonitrile and nitrobenzene; $-CN$ and $-NO_2$ are *o,p*-directors and the partial rate factors are greater than unity.

Table 2. Isomer distributions and partial rate factors in phenylation with (a) phenyl radical and (b) phenyl cation

(a) Phenyl Radical (from I in a non-acidic medium)[3]

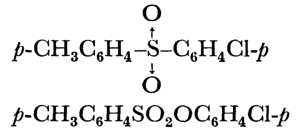
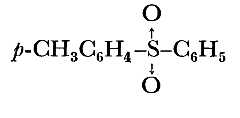
Substrate	Isomer distribution (%)			Partial rate factors		
	o	*m*	*p*	*o*	*m*	*p*
Anisole	65.8	21.4	12.8	4.79	1.56	1.89
Ethylbenzene	53.5	30.1	16.4	2.02	1.14	1.24
Chlorobenzene	60.6	22.8	16.6	3.63	1.36	1.99
Benzonitrile	49.4	15.6	35.0	5.20	1.66	7.38
Nitrobenzene	65.7	8.3	26.0	11.07	1.42	8.72

(b) Phenyl Cation (from I in an acidic medium)[2]

Substrate	Isomer distribution (%)			Partial rate factors		
	o	*m*	*p*	*o*	*m*	*p*
Anisole	74.7	5.0	20.3	2.66	0.18	1.45
Ethylbenzene	53.8	21.7	24.5	1.32	0.56	1.20
Chlorobenzene	71.6	8.0	20.4	0.59	0.08	0.34
Nitrobenzene	26.0	68.9	5.1	0.08	0.20	0.03

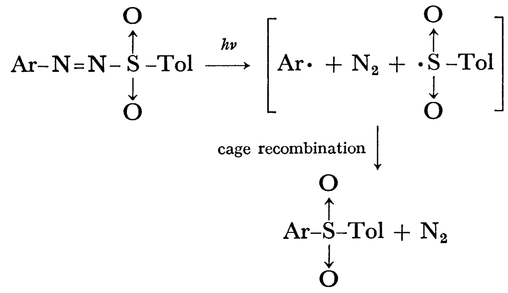
In order to determine the mechanism of photolysis of phenylazo sulfones, photochemical and thermal decompositions of *p*-chlorophenylazo *p*'-tolyl sulfone (II) in benzene were investigated. The products are shown in Table 3. Although II absorbs at 226 (ε=29000), 305 (ε=15000) and 430 nm (ε=190), the results of photo-

Table 3. Products of decomposition of *p*-chlorophenylazo *p*'-tolyl sulfone

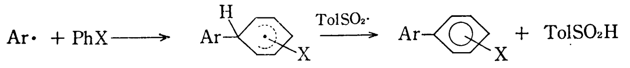
Product	Yield (mol/100 mol-II)		
	Photolysis		Thermolysis (in the presence of CaO)
	Run 1	Run 2	
$p\text{-}CH_3C_6H_4SO_3H$	25.1		12.6
$p\text{-}CH_3C_6H_4SO_2SC_6H_4CH_3\text{-}p$	3.3	3.6	3.6
 $p\text{-}CH_3C_6H_4\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}C_6H_4Cl\text{-}p$	15.6	15.0	1.6
$p\text{-}CH_3C_6H_4SO_2OC_6H_4Cl\text{-}p$	2.1	4.4	4.7—12.3
$p\text{-}ClC_6H_4C_6H_5$	34.2	38.1	47.6
$p\text{-}ClC_6H_4\text{-}N{=}N\text{-}C_6H_4Cl\text{-}p$	0.04		6.2
 $p\text{-}CH_3C_6H_4\text{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{-}C_6H_5$	less than 1.0(glc)		
Polymer sulfone	(10.8 wt%)	(6.1 wt%)	(13.0 wt%)
$p\text{-}CH_3C_6H_4SSC_6H_4CH_3\text{-}p$	trace		
$p\text{-}ClC_6H_4C_6H_4C_6H_4Cl\text{-}p$	0.2	0.3	
A hydrazine derivative	0	0	(19.4 wt%)

lyses in a quartz vessel and in a pyrex vessel were similar. Thus, the absorption at 430 nm is mainly responsible for the photolysis.

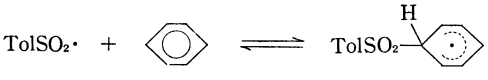
Formation of the products of the photolysis of II can be explained by the following scheme.



$$\mathrm{Ar{-}N{=}N{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}{-}Tol} \xrightarrow{h\nu} \left[\mathrm{Ar\cdot} + \mathrm{N_2} + \cdot\mathrm{\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}{-}Tol}\right] \xrightarrow{\text{cage recombination}} \mathrm{Ar{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}{-}Tol} + \mathrm{N_2}$$



Yields of phenyl *p*-chlorophenyl sulfone were very small both in photolysis and thermolysis (less than 1 mol % by glc). This indicates that *p*-toluenesulfonyl radical functions only as a hydrogen abstractor. However, it is possible that the sulfonyl radical adds to benzene, forming a sulfonylcyclohexadienyl radical in the following equilibrium.



Such a possibility is not rejected by the experimental results. It is likely that the life of the sulfonyl radical is prolonged by existence of such equilibrium.

When a sulfonyl radical abstracts hydrogen, a sulfinic acid should be produced. However, a sulfinic acid was not detected in the reaction mixture, though a sulfonic acid and a thiolsulfonate were found. It is known that a sulfinic acid disproportionates easily, forming such products.[4]

$$3\,p\text{-}\mathrm{TolSO_2H} \longrightarrow p\text{-}\mathrm{TolSO_3H} + p\text{-}\mathrm{TolSO_2S\text{-}Tol}\text{-}p$$

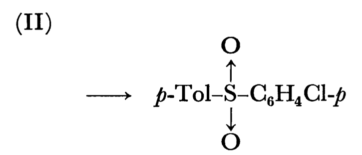
Isomer distributions and partial rate factors in phenylation of substituted benzenes, shown in Table 1, are in general similar to those of thermal homolysis shown in Table 2(a), and are characteristic of free radical reactions. However, the values are somewhat different and the differences in partial rate factors being fairly large in the case of benzonitrile and nitrobenzene.

It is known that sulfones undergo photolysis in aromatic solvents, yielding biphenyls,[5] and occurrence of such photolysis could be the cause for the difference in partial rate factors. However, when a benzene solution of phenyl *p*-tolyl sulfone was degassed and irradiated for 45 hr, the yield of biphenyl was only 9%. Since the yield of *p*-chlorophenyl *p'*-tolyl sulfone in the photolysis of II was only 15%, photolysis of the sulfone so produced cannot influence the partial rate factors greatly.

Photolysis was carried out at room temperature (20°C), and thermolysis at 80°C. However, it was established by a previous investigation that isomer distribution and partial rate factors in phenylation by phenyl radical do not vary much with the reaction temperature.[3] Thus, the cause for the difference in phenylations by photolysis and thermal homolysis cannot be the difference in reaction temperature.

A most probable explanation for the difference is as follows. In photolysis, the azosulfone is photolyzed by the n-π^* transition, yielding free phenyl radical and free *p*-toluenesulfonyl radical; the free phenyl radical adds to a substituted benzene, yielding phenylcyclohexadienyl radical. In thermal homolysis, a π-complex between the azosulfone and the solvent is formed prior to the cleavage of the C–N and S–N bonds, and the bond between phenyl radical and the solvent molecule is formed concertedly with the cleavage of the C–N and S–N bonds.

The yield of *p*-chlorophenyl *p'*-tolyl sulfone in photolysis was very much greater than that in thermolysis as shown in Table 3. The difference can also be explained in terms of the free phenyl radical in the photolysis and the solvated free phenyl radical in the thermolysis. In photolysis, free *p*-chlorophenyl radical and free *p*-toluenesulfonyl radical recombine in a solvent cage and form the sulfone in a fair yield.

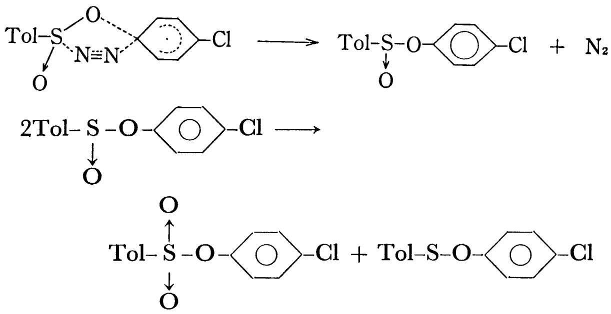


$$p\text{-}\mathrm{TolSO_2{-}N{=}N{-}C_6H_4{-}Cl}\text{-}p \longrightarrow [p\text{-}\mathrm{TolSO_2\cdot\ N_2\ \cdot C_6H_4Cl}\text{-}p] \longrightarrow p\text{-}\mathrm{Tol{-}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}{-}C_6H_4Cl}\text{-}p$$

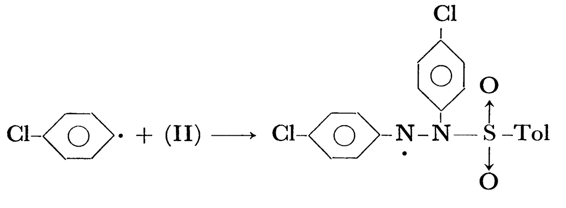
(II)

In the thermolysis, cleavages of the C–N and S–N bonds are aided by formation of weak bonds between solvent molecules and the radicals being produced, and therefore the yield of the sulfone is much smaller.

Formation of *p*-chlorophenyl *p'*-toluenesulfonate cannot be easily explained. A plausible route is disproportionation of *p*-chlorophenyl *p'*-toluenesulfinate formed in the following way.



Formation of 4,4'-dichloroazobenzene can be explained in terms of the addition of *p*-chlorophenyl radical to the starting azosulfone.



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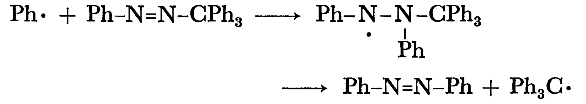
[4] J. L. Kice and K. W. Bowers, *J. Amer. Chem. Soc.*, **84**, 605 (1962).

[5] N. Kharasch and A. I. A. Khodair, *Chem. Commun.*, **1967**, 98.

The reaction is analogous to the attack of phenyl radical to phenylazotriphenylmethane. In both cases, a less stable radical adds to the azo bond, and a more stable radical is released.



$$\mathrm{Ph\cdot + Ph{-}N{=}N{-}CPh_3 \longrightarrow Ph{-}\underset{\cdot}{N}{-}\underset{\mathrm{Ph}}{\underset{|}{N}}{-}CPh_3 \longrightarrow Ph{-}N{=}N{-}Ph + Ph_3C\cdot}$$

Experimental

Materials. Phenylazo *p*-tolyl sulfone was synthesized by the method described previously.[3] UV, λ_{max} (hexane) 221 nm (ε, 19000), 287 nm (ε, 16000), 432 nm (ε, 150). *p*-Chlorophenylazo *p'*-tolyl sulfone (II) was synthesized by the reaction between *p*-chlorobenzenediazonium chloride and sodium *p*-toluenesulfinate in water, and recrystallized from methanol; mp 118.5—119.0°C (decomp.). UV, λ_{max} (hexane) 226 nm (ε, 29000), 305 nm (ε, 15000), 430 nm (ε, 190).

Determinations of Biaryls Formed by Photolysis of I. About 3 mmol of I was dissolved in a mixture of 1/8 mol each of benzene (or chlorobenzene) and a substituted benzene, and the solution was degassed by the freezing-evacuation technique. The solution was irradiated with a high-pressure mercury lamp for 15—60 hr (irradiation was continued for 5 hr after the evolution of nitrogen ceased). An internal standard (bibenzyl) was added, and the reaction mixture was washed with water, a 5% sodium carbonate solution and then concentrated by evaporation of the solvent. When azobenzene formed in a small yield interfered glc determinations, it was removed by reduction with zinc and hydrochloric acid in methanol. The amounts of biaryl isomers were determined with a Hitachi K-53 Flame Ionization Gas Chromatograph (Apiezon L column, 4 m).

Products of Photolysis of p-*Chlorophenylazo* p'-*Tolyl Sulfone (II) in Benzene.* A solution of II (35.4 mmol) in benzene (450 m*l*) was photolyzed with a high-pressure mercury lamp for 25.5 hr at 20°C under nitrogen. A considerable amount of *p*-toluenesulfonic acid precipitated. After the reaction mixture was washed with a 5% sodium carbonate solution and then concentrated, the products in the residue were separated by elution chromatography on alumina or Florisil. Products separated were rechromatographed when necessary. Each product was identified by its mp, IR and/or NMR spectra.

The sodium carbonate extracts were concentrated under reduced pressure, made weakly acidic by addition of hydrochloric acid, and the *p*-toluenesulfonic acid in the solution was precipitated as its *S*-benzylisothiuronium salt. No *p*-toluenesulfinic acid was detected.

4,4'-Dichloroazobenzene was determined by use of its absorption at 444 nm (ε, 880) after column-chromatographic separation.

Products of Thermal Decomposition of II in Benzene. A solution of II (35.4 mmol) in benzene (600 m*l*) containing CaO powder (5.4 g) was kept at 70°C for 82 hr under nitrogen. The products of decomposition were analyzed by the procedure described for photolysis.

By a separate experiment, the rate of decomposition of II was determined (II, 3.260 mmol; benzene, 60 m*l*; CaO, 0.54 g). The rate of evolution of nitrogen showed that rate constant k is equal to 2.1×10^{-5} sec^{-1} at 70.0°C.