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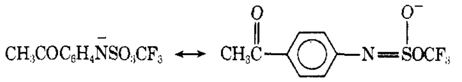

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Behavior of the Sulfoxide Group on the Nitration of Some Aryl Derivatives

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The product composition and the dependence of the reaction rates on acidity for the nitration of methyl phenyl sulfoxide in 83-100% sulfuric acid have been determined. The observed behavior compared with that of diphenyl sulfoxide and the dimethylphenylsulfonium ion shows that the species B and BH^+ present at equilibrium are involved in the nitration of sulfoxide compounds. Relative reactivities and partial rate factors of the conjugate acid form of the substrates are calculated at high acid concentrations.

The substituent effect of the sulfoxide group in an aromatic system can be expected to derive from polar and conjugative interactions. For methyl phenyl and diphenyl sulfoxide, the study of the nature of the interactions with the phenyl ring and the relative importance of their effects on the nitration reaction present some difficulties, in part because of the unreactivity of these substrates in such solvents as nitroethane and acetic acid, and in part because of the oxidation reaction ($>SO \rightarrow >SO_2$) occurring in acetic anhydride or aqueous sulfuric acid below the range of 80%.[1]

Working at high concentrations of sulfuric acid, a substitution reaction has been observed and the isomeric composition of nitro compounds formed is dependent on medium acidity.[1,2]

There is evidence that sulfoxides in acid solution are protonated at the oxygen atom.[3,4] Thus the interpretation of substituent effects for nitrations in concentrated sulfuric acid needs a preliminary investigation concerning the nature of the reactive species involved in the reaction.

We now consider the kinetics of the nitration of methyl phenyl sulfoxide over the range 83-100% sulfuric acid and the acidity dependence of the substitution reaction compared to that observed for diphenyl sulfoxide[2] and dimethylphenylsulfonium ion.[5]

Results and Discussion

In the range 83-100% sulfuric acid, methyl phenyl sulfoxide reacts with nitric acid to give products whose nature and composition are a function of acid concentration (Table I). At lower acidities oxidation (sulfoxide → sulfone) and nitration reactions are observed; at higher acidities only nitration occurs and the isomeric composition of nitro derivatives in the whole range studied shows predominant meta substitution which increases with the acidity of the medium.

The values of second-order rate coefficients (k_2) for the nitration reaction are reported in Table II together with the calculated rate coefficients for attack at one ortho (k_o), meta (k_m), and para (k_p) position.

Comparison of the results in Tables I and II with those obtained for diphenyl sulfoxide[2] shows that the stoichiometric rate coefficients for the -SOMe group are less than those for the -SOPh group by a factor of *ca.* 10; however, both substrates are very similar in the dependence of the product composition on acidity. Thus the meta/para ratio increases for PhSOMe and Ph_2SO respectively by a factor of 5.7 and 5 as the medium acidity increases.

The shape and slopes of the rate profile of methyl phenyl sulfoxide in the range 83-100% are reported in Figure 1 together with those of diphenyl sulfoxide and dimethylphenylsulfonium ion. The values of the slopes for methyl phenyl sulfoxide (+0.265 and −0.0507) below and above 90% sulfuric acid are close to the value observed for diaryl sulfoxide[2] at the lower acidities and to that for the dimethylphenylsulfonium ion[5] at the higher acidities.

To aid in the identification of the reacting species, the experimental rate profile for the nitration of methyl phenyl sulfoxide is compared in Figure 2 with that calculated for reaction of the free base.

The calculated curve has been obtained using that of the dimethylsulfonium ion as a model and by applying a correction for the variation of the conjugated acid corrected for the free base concentration with acidities. Since the sulfoxides cannot be regarded as Hammett bases,[3,4] the $[BH^+]/[B]$ ratios have been calculated by the method of

Table I
Oxidation and Nitration Products of Methyl Phenyl Sulfoxide in Aqueous Sulfuric Acid at 25°

H_2SO_4, %	Oxidation, %[a]	Nitration, %[b]	Nitromethyl phenyl sulfoxide, % o-	% m-	% p-	m-/p-
82.5	56	44	10.1	63.7	26.2	2.43
83.2	47	53	9.7	65.0	25.3	2.57
83.9	42	58	9.3	66.3	24.4	2.70
85.0	26	74	8.8	68.2	23.0	2.96
85.2	23	77	8.7	68.6	22.7	3.02
87.6		100	7.5	73.0	19.5	3.74
88.4		100	7.1	74.5	18.4	4.05
90.3		100	6.2	77.7	16.1	4.83
91.4		100	5.7	79.6	14.7	5.41
93.3		100	4.8	82.9	12.3	6.75
93.4		100	4.7	83.2	12.1	6.87
94.7		100	4.1	85.4	10.5	8.17
96.1		100	3.4	88.0	8.6	10.27
98.4		100	3.3	90.2	6.5	13.88

[a] Methyl phenyl sulfone. [b] o-, m-, p-nitrophenyl methyl sulfoxides.

Yates.[6] Comparison of the experimental rate profile for methyl phenyl sulfoxide with that of sulfonium ion (Figure 1) and that for the hypothetical free base (Figure 2) shows that experimental results accord well with reaction through the conjugate acid. However there is one difficulty in the assumption that reaction occurs entirely through the conjugate acid. This arises from the variation of the isomer distribution with acidity; variation is observed also in the nitration of diphenyl sulfoxide. In the nitration of methyl phenyl sulfoxide, the values of the slopes for nitration below and above 90% sulfuric acid are +0.275 and −0.041 for meta substitution and +0.240 and −0.103 for para substitution; the corresponding values for the nitration of diphenyl sulfoxide are +0.267 and −0.057 for meta substitution and +0.237 and −0.101 for para substitution. The greater slope of para substitution compared to meta at high acidities suggests that part of the reaction still involves the free base, but the rate profiles in Figures 1 and 2 suggest that this is not a major part.

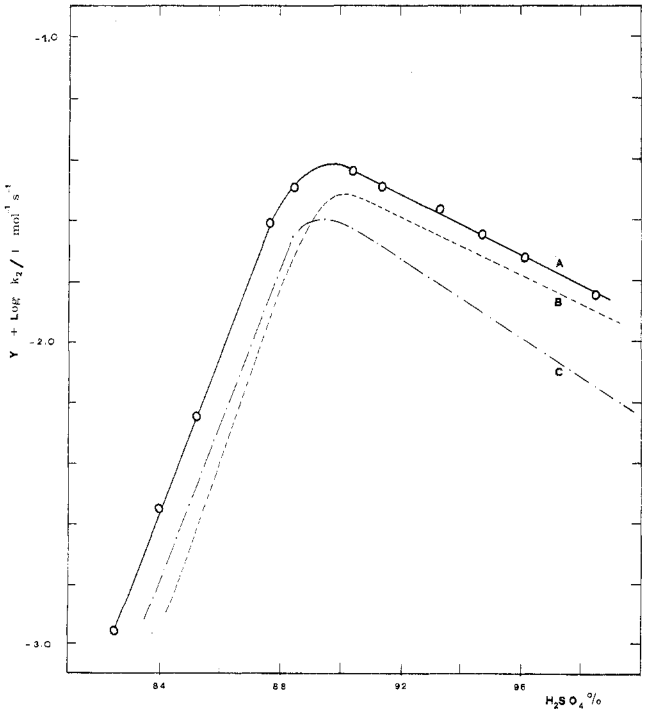

Figure 1. Rate profiles and slope values for the nitration of (A) methyl phenyl sulfoxide (+0.265, −0.0507); (B) dimethylphenylsulfonium methylsulfate (+0.284, −0.047); (C) diphenyl sulfoxide (+0.260, −0.064). Values of the constant Y are $A = 0$; $B = 0$; $C = +1$.

Table II
Second-Order Rate Coefficients (l. mol^{-1} sec^{-1}) for Nitration of Methyl Phenyl Sulfoxide in Aqueous Sulfuric Acid at 25°[a]

H_2SO_4, %	10^4k_2	10^5k_o	10^5k_m	10^5k_p	k_p/k_m
82.5	1.10	0.55	3.49	2.88	0.82
83.9	2.83	1.33	9.39	6.91	0.73
85.2	5.69	2.48	19.51	12.91	0.66
87.6	24.58	9.28	89.66	47.90	0.53
88.4	32.33	11.56	120.40	59.50	0.49
90.3	36.90	11.44	143.40	59.41	0.41
91.4	32.16	9.20	128.00	47.80	0.37
93.4	28.01	6.62	116.50	33.90	0.29
94.7	23.32	4.79	99.60	24.39	0.24
96.1	19.06	3.25	83.86	16.33	0.19
98.4	14.13	2.34	63.69	9.18	0.14

[a] k_o, k_m, and k_p have been calculated from the isomeric distribution given in Table I. The Arrhenius parameters calculated at 98.4% sulfuric acid are $E_a = 12.4$ kcal mol^{-1}, log $A = 6.22$ l. mol^{-1} sec^{-1}, and $\Delta S^* = -30.1$ cal mol^{-1} °K^{-1}.

A mechanistic encounter rate criterion[7] for methyl phenyl sulfoxide in 98% sulfuric acid was also adopted and log k_2 (encounter) (4.90) was compared with the observed value (−2.81). At the same acidity the corresponding values for the diphenyl sulfoxide are 6.03 and −2.12. These results for the compounds examined indicate that nitration can occur *via* the free base. Indeed, for the arylmethyl relative to diaryl derivative, one can expect that the higher basicity constant[3] should decrease the proportion of reaction through the free base, and this is consistent with the smaller proportion of para substitution observed.

We assume therefore that, for both substrates, reaction occurs mainly through the conjugate acid but with a small contribution, which decreases with acidity, from reaction through the free base. The rate profiles suggest that this contribution should be very small at high acidities, and,

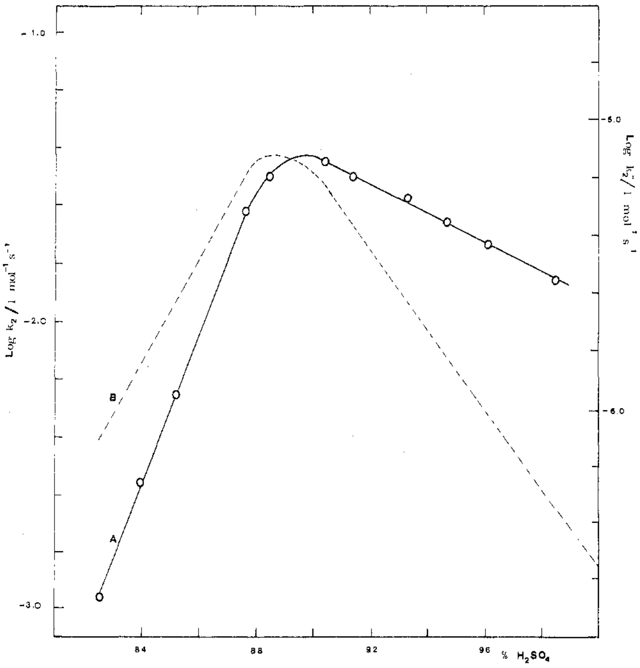

Figure 2. A, the experimental rate profile [log k_2 (obsd)] for the nitration of PhSOMe; B, expected rate profile [log k_2'' (calcd)] for the free base, calculated following $k_2'' = C\,(k_2/h_0)$.

for the purpose of calculating relative reactivities and partial rate factors for the reaction in *ca.* 98% sulfuric acid, the free base component has been ignored. The results are given in Table III. The comparison between the $PhSMe_2^+$ ion and the conjugate acids of sulfoxides shows small differences on the reactivity compared to overall deactivating influence of the positive pole.

However, on the cation of sulfoxides the change from $-S(OH)Me^+$ group to $-S(OH)Ph^+$ increases the reactivity by a factor of *ca.* 10, and in these compounds the amount of para increases more than the amount of meta nitration. This behavior suggest a progressively decreasing influence of π(d-p) overlap relative to the electrostatic deactivating effect in the sequence $PhSMe_2^+$, $PhS(OH)Me^+$, $PhS(OH)Ph^+$.

Experimental Section

Materials. *m*-Nitrophenyl methyl sulfoxide was prepared by nitration of methyl phenyl sulfoxide (0.1 *M*) with nitric acid (0.15 *M*) in 98% sulfuric acid at 25°. After 3 hr the reaction mixture was quenched in cold water, neutralized with sodium hydroxide, and extracted with chloroform. Drying and evaporation of the solvent gave the *m*-nitro derivative as the larger product of the reaction (*cf.* Table I). The compound was purified by crystallization from 95% ethanol, mp 117–118° (lit. mp 117–118° obtained by oxidation of *m*-nitrophenyl methyl sulfide[8]).

All the other compounds were prepared and purified as described in the literature and shown to be pure by glc and tlc. Sulfuric and nitric acid were Analar reagents. For all nitrations 16.2 *M* nitric acid was used. Solutions of sulfuric acid required as reaction media for kinetic or isomeric runs were obtained by diluting concentrated sulfuric acid and were standardized by titration with 0.1 *N* sodium hydroxide (normex) using an automatic titrator (Amel-235).

Kinetics. In order to avoid decomposition,[9,10] a concentration range of sulfuric acid up to 99% was used; also methyl phenyl sulfoxide was dissolved in thermostated solvent immediately before the start of the nitrations. The general procedure was followed as described previously[2] for the nitration of diphenyl sulfoxide. The extent of reaction was determined in a Hitachi Perkin-Elmer EPS 3T sepctrometer from the variation in the optical density at 300 nm in samples of the reaction mixture, quenched at suitable times in cold aqueous 0.1 *M* sodium hydroxide.

At this wavelength and at concentrations used, absorptions of other compounds are negligible; appropriate corrections were made when methyl phenyl sulfone was present. Nitro derivatives are proportional to optical densities; the latter do not vary with the base concentration (0.2–0.02 *N*) or with the time (up to 2 hr).

In all cases good second-order kinetics during individual kinetic runs have been observed and the second-order rate coefficient at a given acidity was shown to be independent of the initial concentrations of the reactants when varied over the range 0.0454–0.0986 *M*. Details of the integrated rate coefficients through a typical kinetic run are given in Table IV.

Total amount of nitro derivatives was calculated as described previously for the nitration of diphenyl sulfoxide.[2] The values of extinction coefficients of *o*-, *m*-, and *p*-nitrophenyl methyl sulfoxides at 300 mm derived from measurements on 0.1 *N* sodium hydroxide solutions of the pure isomers were as follows: ortho, 3302; meta, 1398; para, 5305.

Product Analysis. Nitration mixtures, some of these residual solutions from the kinetic runs, were poured into cold water, neutralized with aqueous sodium hydroxide at low temperature, and rapidly extracted with chloroform. In this way, possible alkaline cleavage of nitrophenyl methyl sulfoxides to nitrophenols can be avoided. The presence of *o*-, *m*-, and *p*-nitrophenyl methyl sulfoxides was ascertained by glc and tlc analysis together with methyl phenyl sulfone on the range 82–87% sulfuric acid. Samples of solutions were analyzed by glc analysis in a Hewlett-Packard 5700 A instrument and the oxidation-nitration composition was determined with a 120-cm column packed as reported previously.[2] Tests with mixtures of known composition showed partial separation of the three mononitro compounds by glc analysis; the separation was complete for the corresponding amino sulfides. The isomeric compositions of nitro compounds were then evaluated after quantitative reduction of the nitration solutions with stannous chloride and gaseous hydrogen chloride as reported elsewhere.[2]

Table III
Reaction Rates Relative to Benzene and Partial Factors for Nitration of Methyl Phenyl and Diphenyl Sulfoxides in Aqueous Sulfuric Acid at 25°

Compd	Expected reactive specie	Relative rate	$10^9 f_o$	$10^9 f_m$	$10^9 f_p$	$\frac{\log f_p}{\log f_m}$	$\frac{\log f_o}{\log f_m}$
$PhSMe_2^+$		3.98×10^{-9} [a]	0.26	11.2	0.94	1.13	1.21
PhSOMe	*c*	4.57×10^{-9} [b]	0.45	12.4	1.78	1.11	1.18
Ph_2SO	*c*	2.19×10^{-8} [b]	1.15	27.4	8.53	1.06	1.18

[a] Calculated at 98.7% H_2SO_4 from the relative rate with respect to $PhNMe_3^+$: N. C. Marziano, E. Maccarone, and R. C. Passerini, *Tetrahedron Lett.*, 17 (1972). [b] Calculated at 98.7% H_2SO_4 from the relative rate with respect to $PhSMe_2^+$ using observed rate constants. [c] Conjugate acid.

Table IV
Nitration of Methyl Phenyl Sulfoxide in 91.4% Sulfuric Acid at 25° [a]

Time, sec	300	420	540	660	780	900	1080	1200	1320	1560	1800	2100	2280	2700	3060	3600
OD (300 nm)[b]	0.200	0.298	0.380	0.432	0.488	0.551	0.644	0.689	0.737	0.841	0.917	1.028	1.082	1.200	1.269	1.395
$10^2 M$[c]	0.479	0.714	0.910	1.034	1.168	1.319	1.542	1.650	1.765	2.014	2.196	2.462	2.591	2.874	3.039	3.341
$10^4 k_2$, l. mol^{-1} sec^{-1} [d]	30.66	33.81	34.45	32.88	32.05	32.11	32.59	32.00	31.74	32.18	31.56	32.29	32.02	32.07	31.14	31.58

[a] [PhSOMe] = 5.67×10^{-2} *M*; [HNO_3] = 9.86×10^{-2} *M*. [b] Dilution factor before measurement of OD = 50. [c] Total concentration of *o*-, *m*-, and *p*-nitro derivative calculated as reported: N. C. Marziano, E. Maccarone, and R. Passerini, *J. Chem. Soc. B*, 745 (1971). [d] Average k_2 = 32.16×10^{-4} l. mol^{-1} sec^{-1}.

o-, *m*-, and *p*-aminophenyl methyl sulfides were determined by glc analysis carried out using the same column described above and reported before.[2]

The reduction process, as the glc analysis, was shown to be satisfactory (±2%) by the use of synthetic mixtures of pure isomers. Oxidation–nitration composition as isomeric compounds values are an average of three gas chromatographic analysis and the areas are corrected by calculated correction factors.

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Registry No.—Methyl phenyl sulfoxide, 1193-82-4; diphenyl sulfoxide, 945-51-7.

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Reaction of Aromatic Substrates with Sulfonyl Nitrenes[1a]

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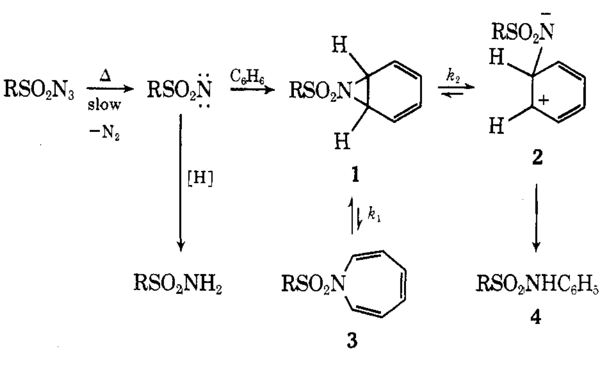
The thermolysis of methanesulfonyl azide in aromatic solvents bearing electron-withdrawing substituents has been studied quantitatively in the presence and absence of compounds known to catalyze singlet → triplet interconversions. The results show that the singlet sulfonyl nitrene formed initially drops to the triplet to a certain extent: the singlet adds to the aromatic nucleus to give a benzaziridine intermediate that ring opens to yield the meta-substituted anilide predominantly. The triplet attacks the nucleus as expected of a highly electrophilic diradical and leads mainly to the ortho isomer. In nitrobenzene, the nitrene behaves only as the electrophilic triplet and, in addition to nitroanilides, yields products in which the nitro group has been displaced.

The thermal decomposition of sulfonyl azides in aromatic solvents, which was first studied by Bertho, Curtius, and Schmidt,[1b] occurs slowly at 120°, is unimolecular,[2] and leads to singlet nitrenes.[3] This is followed by an addition to the aromatic nucleus to give a benzaziridine intermediate (1), with ring opening of the latter to form the observed *N*-sulfonanilides (4)[3] *via* 2 being a relatively fast, thermodynamically controlled process, and ring opening to form the azepine (3) being an even faster kinetically controlled reaction.[4] The unsubstituted primary sulfonamides, products of hydrogen abstraction by the nitrene, are also formed in these reactions.



The isomer ratios and relative reactivities[3] in the reactions of methanesulfonyl nitrene with toluene, anisole, and chlorobenzene could be explained readily on the basis of the above mechanism. Electron-donating substituents facilitate addition to the aromatic nucleus while electron-withdrawing ones slow the addition down. The substituent determines the direction of ring opening 1 → 2 by whether or not it can stabilize the developing positive charge in the aromatic nucleus in the product-, but not rate-, determining step. Since formation of a σ complex is not rate determining, partial rate factors have no physical significance in this reaction[3] and are not considered here.

It would then be predicted that an electron-withdrawing substituent would not only deactivate the nucleus but would also direct the ring opening of the aziridine ring to favor formation of the meta isomer. Confirmation of this appeared to be forthcoming from studies of the benzenesulfonamidation of methyl benzoate and benzoyl chloride using benzenesulfonyl azide, when the isomer ratios were reported to be ortho, 43%; meta, 54%; para, 3%; and meta, 100%, for these two substrates, respectively, and the total rate ratio $^{CO_2Me}{}_{H}K = 0.38$.[5] Since these latter data were obtained from fractional distillation experiments and we had found in earlier work[3] that these led to poor quantitative results, it was felt that the reaction of sulfonyl nitrenes with aromatic nuclei bearing electron-withdrawing substituents should be reinvestigated quantitatively using gas–liquid chromatography (glc). Once