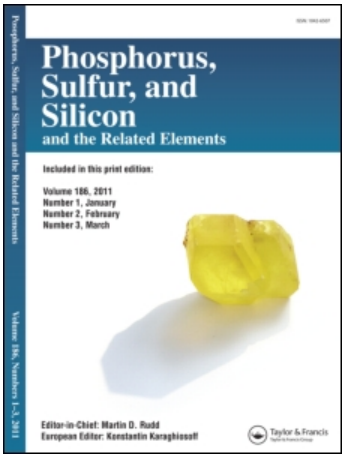

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SULFENAMIDES AND SULFINAMIDES VII. REACTIONS OF ARYL SULFINAMIDES WITH DIPHENYLPICRYLHYDRAZYL FREE RADICAL

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In common with the sulfenamides, hydrogen abstraction is postulated as the first step in reactions of aryl sulfinamides with the stable diphenylpicrylhydrazyl free radical. However, marked differences between the reactions of the two classes are established, with rates and extents of reaction controlled by the oxidation level of the sulfur atom. Reversibility of the sulfinamide reaction is discussed.

Key words: Sulfenamides; sulfinamides; diphenylpicrylhydrazyl free radical; sulfinyl-nitrogen bond; reaction reversibility.

INTRODUCTION

The earlier discussion[1] of the dehydrogenating capacity of the diphenylpicrylhydrazyl free radical (DPP·) drew attention to a strong capability for removal of hydrogen attached to nitrogen as in primary[2] and secondary[3] amines. The reaction with aryl sulfenamides (ArSNHAr) was found subject to electronic and steric control by substituents but only with 2-substitution in the aniline residue was complete inhibition noted.[1] This was attributed to steric hindrance.

The influence of the oxidation level of the sulfur atom on its capability to relay electronic effects in the aryl sulfenamides[4] and sulfinamides (ArSONHAr),[5] previously discussed in relation to their pKa values, is now examined with respect to the reaction of sulfinamides with DPP·.

RESULTS AND DISCUSSION

Figure 1 shows that, initially, reactions are considerably faster than with sulfenamides but do not proceed to completion. Instead they are seen to come to an equilibrium which is then more slowly upset by decomposition of products. It has been proposed that a driving force of the initial hydrogen abstraction from the sulfenamides lies in the increasing resonance stability of the emergent radical, with the odd electron distributed over two hetero atoms of the S—N group. In the case of the sulfinamides, the odd electron may be distributed over the three atoms of the SO—N group thereby contributing further to emergent radical stability. It has been suggested that the primary stability of an aromatic RSO· radical is almost

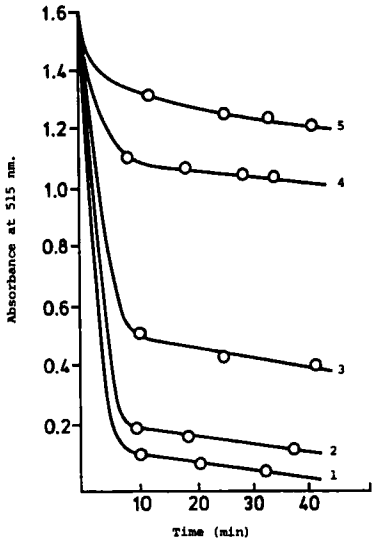


FIGURE 1 Substituent influence on the reaction of diphenylpicrylhydrazyl (DPP·) with aryl sulfinamides (ArSONHAr') in methanol. **1**, Ar=Ar'=C_6H_5; **2**, Ar=C_6H_5, Ar'=4-CH_3—C_6H_4; **3**, Ar=4-CH_3—C_6H_4, Ar'=C_6H_5; **4**, Ar=Ar'=4-CH_3—C_6H_4; **5**, Ar=C_6H_5, Ar'=4-CH_3O—C_6H_4.

entirely associated with delocalization of the odd electron over the SO group and not with delocalization into the aromatic ring.[6,7] It seems likely that this concept would extend further to the nitrogen of the SO—N group.

In contrast to the sulfenamides, substitution with electron donating groups in both aromatic rings of the sulfinamides leads to an apparently anomalous result of a decrease in rate together with a decidedly lesser extent of reaction (Figure 1). Retardation of DPP· reactions with phenols by added DPPH has been established [8,9] and interpreted as due to reversal of the primary hydrogen abstraction. Several factors likely to influence sulfinamide reactions were tested separately. First, by using a constant amount of DPP· with increasing amounts of sulfinamide, it was established that each reaction, although proceeding to a different extent, reached an equilibrium in a similar manner (Figure 2). Increasing proportions of sulfinamide accelerate the reaction and displace the equilibrium position but the reactions with DPP· were incomplete despite the large excess of sulfinamide. Results are in general accord with preliminary results of esr spectroscopy which show that disproportionate amounts of sulfinamide are required to wipe out the DPP· signal.

In a similar manner the influence of product DPPH on the extent of reaction was tested. The inverse relationship (Table I) between the amount of DPPH added and the extent of reaction supports the concept of a back reaction.

The superimposed effect of the electron donating groups may be to promote the back reaction, and hence the equilibrium, by increasing the stability of the emergent sulfinamide radical.

A summary of the influence of the oxidation level of the sulfur atom is shown in Table II. The rate orders show sulfonamide <<<amine < sulfenamide < sulfinamide but care is necessary in interpreting these results which are restricted to a

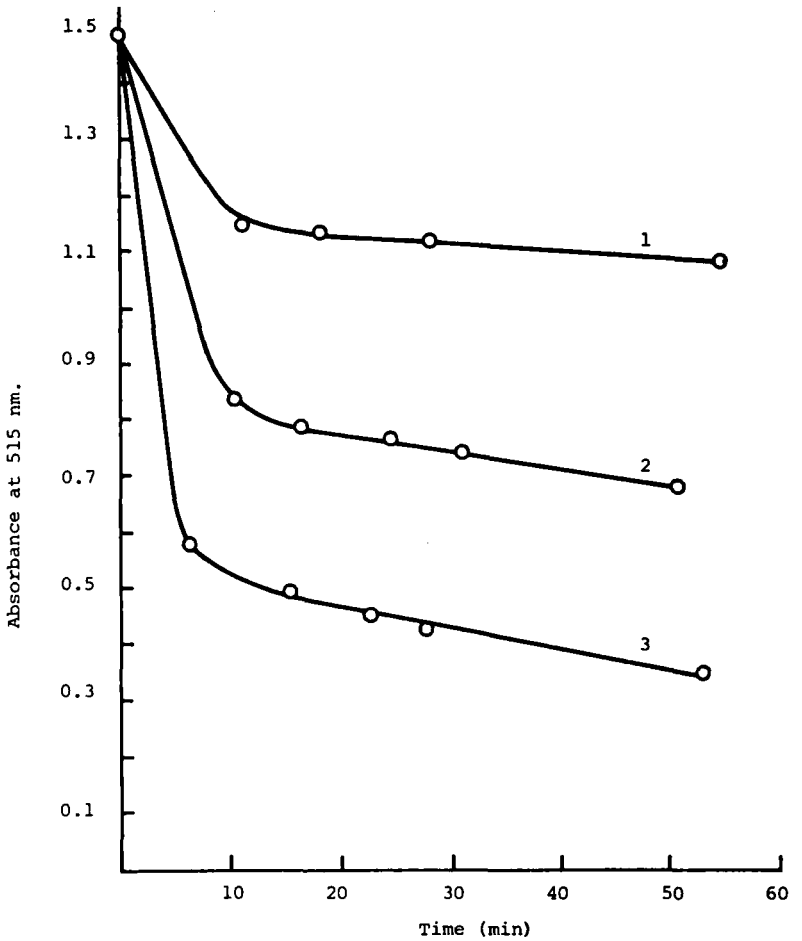


FIGURE 2 Extents of reaction of diphenylpicrylhydrazyl (DPP·, 2×10^{-3} M, 1 ml) with additions of N-(4-methylphenyl-4-methylbenzenesulfinamide (2×10^{-2} M); **1**, 1 ml; **2**, 2 ml; **3**, 3 ml. Solvent methanol. Final volume 10 ml in each case.

TABLE I

Effect of Diphenylpicrylhydrazine (DPPH) on Rate of Reaction of N-(4-methylphenyl)-4-methylbenzene-sulfinamide with Diphenylpicrylhydrazyl (DPP)·).

Added DPPH as % of original DPP·	%DPP·reacted after 60 min	Change in % DPP·reacted
0	31	–
22	26	5
44	21	10
66	15	16

short reaction period. As discussed earlier, the result with the sulfinamide will present the equilibrium position but, subject to substituent influence, reaction with slower acting sulfenamides could continue longer thereby changing its position in the reaction sequence above. This effect is shown in Figure 3.

TABLE II

Reaction of Diphenylpicrylhydrazyl (DPP·) with 4-Methyl-Substituted Aryl Sulfur Amides

Derivative	Absorbance*	Absorbance Loss	Extent of Reaction %
$CH_3—C_6H_4—S—NH—C_6H_4—CH_3$	1.06	0.44	29
$CH_3—C_6H_4—SO—NH—C_6H_4—CH_3$	0.78	0.72	48
$CH_3—C_6H_4—SO_2—NH—C_6H_4—CH_3$	1.50	0	0
$CH_3—C_6H_4—NH_2$	1.12	0.38	25

* Reaction time 30 min; absorbance of DPP· reference solution 1.50.

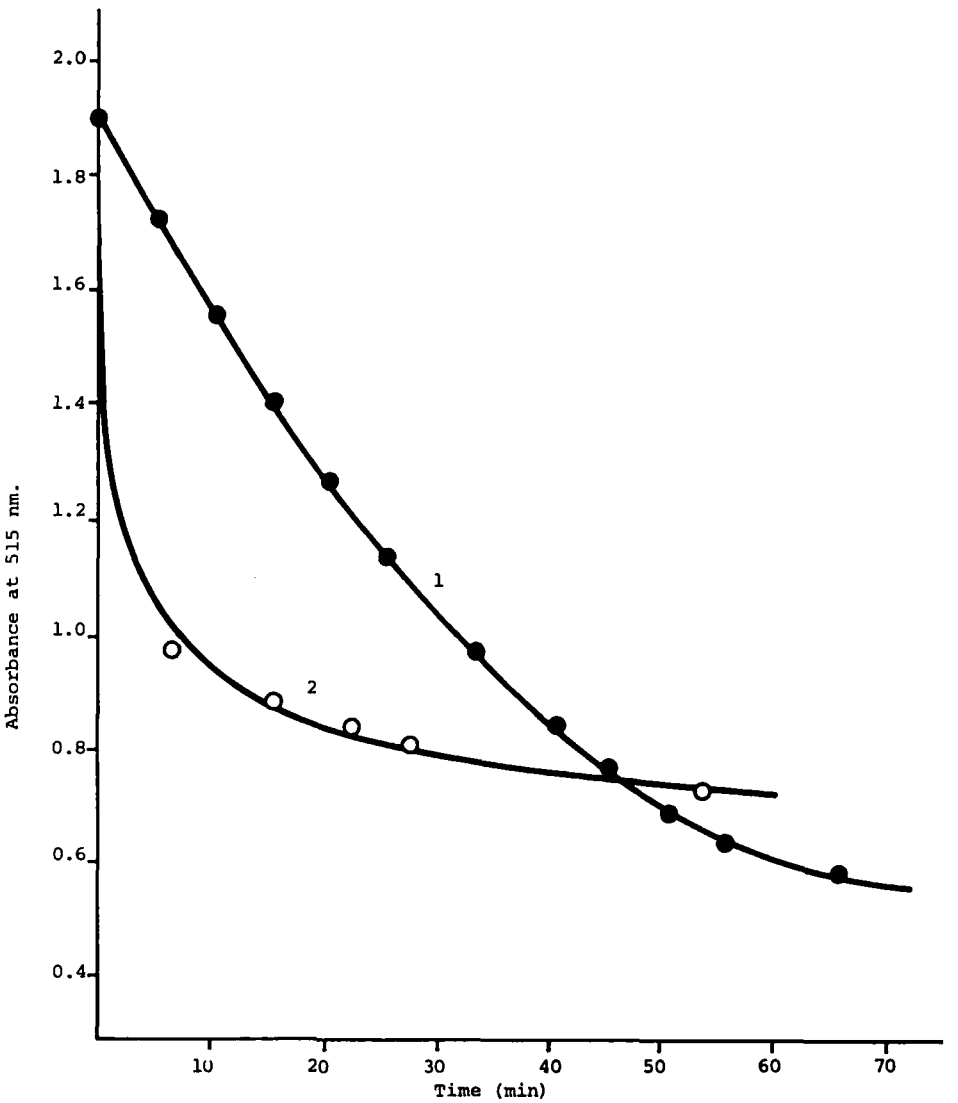
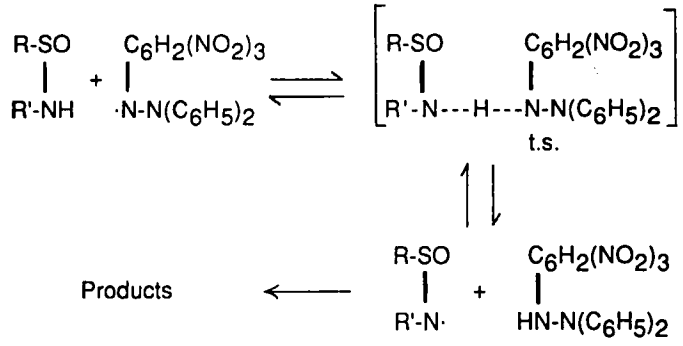


FIGURE 3 Comparison of rates of reaction of **1**, N-(phenyl) benzenesulfenamide and **2**, N-(phenyl) benzenesulfinamide with diphenylpicrylhydrazyl (DPP·).

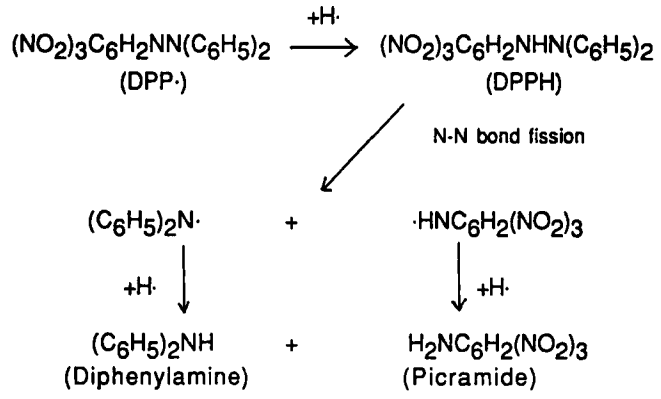
The failure of the sulfonamide to react can be attributed to the full play of the deactivating influence of the sulfone group. Loss of basic properties of the NH group in sulfonamides is long established. The result is akin to the deactivating effect of the nitro group in 4-nitroaniline, which also does not react with DPP·[2]. The reaction of DPP· with primary amines is subject to substituent effects, with rates for aniline derivatives increasing in the order—4-Cl < H < 4-CH_3[2]. If the lack of reactivity of the sulfonamides is attributed to electron withdrawal from the N—H group by the phenylsulfonyl group, this suggests that electron withdrawal by the phenylsulfenyl and phenylsulfinyl groups decreases in that order. The pKa values for the arylsulfenamides are lower than those of the arylsulfinamides[4,5] and hence support this view. Thus conjugative arrangements of the type $O{=}S{-}NH \leftrightarrow {}^{-}O{-}S{=}\overset{+}{N}H$ in the sulfinamides must be limited since reduction in the rate of reaction with DPP· would then be expected as mentioned in the case of the sulfonamides and 4-nitroaniline.

The plateaus introduced into the sulfinamide/DPP· reactions (Fig. 1) must have their origin in a factor other than ease of initial hydrogen abstraction. Therefore a concentration dependent reversibility may be expressed simply as



An essential difference between the present reaction and those of simpler aromatic amines with DPP· lies in the transition state and the stability of the extruded radical both of which contribute to a back reaction. The transition state suggested is similar to that proposed for the phenoxy radical/antioxidant reaction, through which polar influences may be exerted.[9,10]

Products of reaction. The product mixture from a reaction of DPP· with N-(4-methylphenyl)-4-methylbenzenesulfinamide was less extensive than from the sulfenamide[1] but was again characterized by the immediate appearance of a purple color changing over a period of 1 hr to a deep blue. Chromatography on a silica gel column gave five fractions leading to the identification of diphenylamine and DPPH (fractions 1 and 2, total 1.2%), DPPH the main product (fraction 3, 66%) with picramide (fraction 4, 7%) and a blue solid (fraction 5, 7%), obviously products from the reagent in accordance with a sequence of the type:



Comparison of the reaction with that suggested for the sulfenamides[1] shows the greater reactivity of a PhS· radical over the PhSO· radical with potential remaining for nitrene reactions as indicated earlier. Theoretically the sequence leads to equimolar yields of diphenylamine and picramide but the yield of the diphenylamine, (0.3%), suggests further reaction of the intermediate radical or of diphenylamine itself.

Characterization of the blue material presented problems due to its instability. Solutions with absorption peaks at 610 nm and 400 nm faded in the dark, passing through light green to a light brown yellow. Picramide, possibly present as an impurity, was identified. Although thin layer chromatography gave a little more DPPH the amount was not sufficient to explain the spectra. Results suggest that the material is a complex derived from DPP·. Resolution of the question whether the blue products from the sulfenamide and sulfinamide reactions are the same must await more detailed structural work. The products have several properties in common being apparently based on DPP· with retention of free radical character and giving picramide as a decomposition product.

Thus far, concentration has been on the rate of reaction and products from DPP·. Products from decomposition of the sulfinamides have not, as yet, been identified.

EXPERIMENTAL

(i) *Substituent effect on rate and extent of reaction.* To a methanolic solution of the sulfinamide (2×10^{-2} M, 1 ml) was added a solution of DPP· (2×10^{-3} M, 1 ml) and the mixture made to volume (10 ml) and allowed to stand in the dark). A solution of DPP·, similarly prepared, was used as a reference solution. Losses of DPP· based on measurements of absorption at 515 nm are shown in Figure 1.

(ii) *Influence of sulfinamide concentration on extent of reaction.* To aliquots of a solution of DPP· (2×10^{-3} M, 1 ml) were added 1, 2, 3 ml of a methanolic solution of N-(4-methylphenyl)-4-methylbenzenesulfinamide (2×10^{-2} M) and the mixtures then made to volume (10 ml). Extent of reaction was measured against a DPP· reference solution as above. Results are shown in Figure 2.

(iii) *Influence of added DPPH.* To a methanolic solution of DPP· (2×10^{-3} M, 0.9 ml) were added aliquots (0, 2, 4 and 6 ml of a methanolic solution of DPPH (2×10^{-4} M) followed by a methanolic solution of N-(4-methylphenyl)-4-methylbenzenesulfinamide (2×10^{-2} M, 1 ml) and the mixtures then made to volume (10 ml). Results are shown in Table I.

(iv) *Comparison of rates of reaction of DPP· with sulfur amides.* To a methanolic solution of DPP· (2×10^{-3} M, 1 ml) was added a methanolic solution of N-(4-methylphenyl)-4-methylbenzene-sulfinamide (2×10^{-2} M, 2 ml) and the mixture then made to volume (10 ml). Equimolar solutions of equivalently di-methyl-substituted sulfenamide, sulfonamide and of 4-methylaniline were treated similarly. Extents of reactions were measured after 30 min, and results are shown in Table II.

(v) *Products of reaction.* (a) Stoichiometry of DPP·/N-(4-methylphenyl)-4-methylbenzenesulfinamide reaction. To a constant amount of the sulfinamide (0.061 g, 0.25 mmol) in chloroform (5 ml) were added respectively DPP· (0.098 g, 0.25 mmol; 0.147 g, 0.375 mmol; 0.196 g, 0.5 mmol and 0.245 g, 0.625 mmol) each in chloroform (30 ml). Reaction was allowed to proceed for 2 hr before estimation of residual DPP·. Only in the last solution was this found, indicating that reaction required a DPP·/sulfinamide reactant ratio of 2:1.

(b) *Separation of products.* Initial qualitative tlc analysis was performed on silica gel G plates (0.25 mm) using acetone/light petroleum (b.p. 40–60°C)3:97 as developing solvent for 3–4 ascents. For the separation, DPP· (1.97 g, 5 mmol) in chloroform (500 ml) was slowly added with stirring to the sulfinamide (0.61 g, 2.5 mmol) in chloroform (100 ml). A purple color first formed and changed to deep blue over 1 hr. Removal of solvent in vacuo at room temperature gave a residue (2.41 g).

Column chromatography of a portion of the residue (0.3 g), loaded in carbon tetrachloride solution onto a silica gel G column, was performed using the acetone/light petroleum solvent to give the fractions: 1. light brown/yellow viscous oil (2 mg; mixture of diphenylamine and DPPH); 2. light brown/yellow oil (2 mg; mixture of diphenylamine and DPPH); 3. red/brown solid (200 mg; 66%, DPPH); 4. yellow solid (20 mg; 6.6%, picramide); 5. blue solid (20 mg; 6.6%).

Fractions 4 and 5 overlapped with a green band. Lesser amounts of blue, yellow and red bands gave yields too small for further examination. Fraction 5 on tlc gave a weak spot for DPPH together with a spot with the same R_f as picramide. Esr examination of the band indicated free radical properties.

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