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AN ELECTRON SPIN RESONANCE SPECTROSCOPIC STUDY OF SULFONAMIDYL RADICALS

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Sulfonamidyl free radicals, $RSO_2\dot{N}R'$, have previously been invoked as intermediates in a variety of reactions including thermal or photolytic addition and rearrangement reactions of N-halosulfonamides[1] and oxidative intramolecular cyclizations of sulfonamides[2]. However, in the absence of relevant spectral data, no unequivocal conclusions about the electronic structure of sulfonamidyls could be drawn and the radicals have been described in terms of both a σ- or π-electronic ground state[2,3]. In this communication we report the first electron spin resonance (ESR) spectral study of a series of simple aryl- and alkylsulfonamidyl radicals[4]. The transient sulfonamidyls **1a**-**1f** (Table I) were produced by photolyzing the corresponding N-bromo-N-_t_-butylsulfonamides directly in the ESR cavity at -50°C in $CFCl_3$-_n_-pentane (1:1)[5-7].

$$RSO_2N(Br)\text{-}\underline{t}\text{-}Bu \xrightarrow{h\nu} RSO_2\dot{N}\text{-}\underline{t}\text{-}Bu$$

1a-**1f**

The observed hyperfine splitting constants and g-values of **1a**-**1f** are listed in Table I and are completely consistent with the proposed structures. Comparison of the ESR parameters of the sulfonamidyls with those of the corresponding sulfonyl nitroxides[8,9] (Table I) reveals the closely similar A_N-values, the substantially lower g-values of the sulfonamidyls, which are in the expected range for aminyl radicals containing an electron-withdrawing N-substituent[3], and the resolvable hfs due to the nine _t_-butyl protons in the case of **1a**-**1e**.

Table I

Hyperfine Splitting Constants (gauss) and g-Values of Sulfonamidyl Radicals and Sulfonyl Nitroxides[a].

	$RSO_2\dot{N}$-t-Bu					$RSO_2\overset{O}{\overset{|\cdot}{N}}$-t-Bu		
	R	A_N	$A_H^{t\text{-}Bu}$	g		R	A_N	g
1a	p-$CH_3C_6H_4$	13.0	0.62	2.0044	2a	p-$CH_3C_6H_4$	12.0	2.0060
1b	p-$NO_2C_6H_4$	12.9	0.68	2.0046	2b	p-$NO_2C_6H_4$	11.8	2.0060
1c	p-$CH_3OC_6H_4$	12.8	0.59					
1d	CH_3	12.9	0.68	2.0044	2c	CH_3	12.6	2.0060
1e	CD_3	12.9	0.68	2.0044				
1f	$(CH_3)_2CH$	13.0	c	2.0042				

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[a] From RSO_2Cl + t-BuNO + hv, ref. 9. [b] $A_H^{CH_3}$ = 0.34. [c] Not resolved.

The ESR spectrum of 1d is shown in Figure 1 and exhibits further splitting due to long-range hyperfine coupling of the methyl protons across the sulfonyl moiety[10]. Deuteration of this methyl group removes this coupling as shown in the ESR spectrum of 1e (Figure 2).

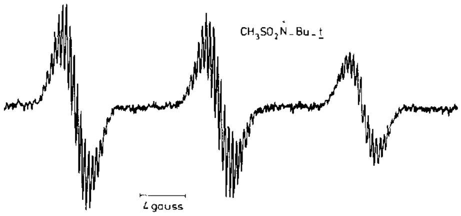

Fig. 1. ESR spectrum of 1d.

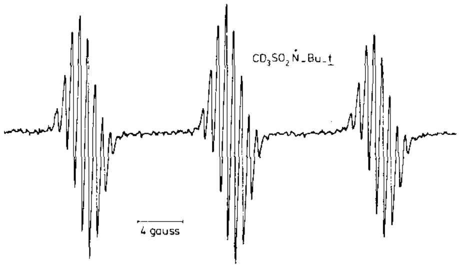

Fig. 2. ESR spectrum of 1e.

The ESR data strongly suggest a π-electronic ground state for 1a-1f. In particular, the relatively low magnitudes of the ^{14}N hyperfine splitting constants furnish evidence for a low s-character of the nitrogen orbital containing the unpaired electron. The g-values lend further support to this conclusion. A π-structure has also been proposed for carboxamidyl radicals ($RCO\dot{N}R'$) on the basis of ESR measurements (A_N ca. 15 gauss)[11] and ^{13}C-CIDNP studies[12]. Since spin delocalization onto the sulfonyl group in the sulfonamidyls is expected to be smaller than onto the carbonyl moiety in carboxamidyls[13], the lower A_N values for the sulfonamidyl radicals (A_N ca. 13 gauss) are not entirely expected. Apparently, both types of amidyl radicals possess slightly different π-configurations. Finally, it is interesting to note that the A_N values of sulfonyl nitroxides (A_N ca. 12 gauss) are markedly larger than those of structurally related acyl nitroxides (A_N ca. 6 gauss). This situation has previously been rationalized[8] by assuming a distortion from planarity at the nitroxide nitrogen atom in the sulfonyl nitroxides.

Further studies are under way to further elucidate the structure of sulfonamidyl radicals.

References and notes.

(1) For a review, see: R.S. Neale, *Synthesis*, 1 (1971).

(2) P.S. Dewar, A.R. Forrester, and R.H. Thomson, *J. Chem. Soc. Perkin I*, 2862 (1972).

(3) W.C. Danen and F.A. Neugebauer, *Angew. Chem. internat. Edit.*, **14**, 783 (1975).

(4) To the best of our knowledge, only ESR parameters for sulfonamidyls of the type *p*-$XC_6H_4\dot{N}SO_2Ar$ (**3**) have been reported previously [e.g., if X=NMe_2, Ar=C_6H_5: $A_{N(1)}$=6.2, $A_{N(2)}$=4.2, A_H=6.2 (2 ortho-H), A_H=2.1 (2 meta-H), A_H=4.2 gauss (6 methyl-H), g=2.0031]. See: R. Istratoiu, J. Pascaru, and A.T. Balaban, *Z. Naturforschung*, **28B**, 543 (1973). These ESR data are not easily reconcilable with those of **1a**-**1f**. However, this may be a consequence of "push-pull" electronic effects in **3**.

(5) The spectra were recorded with a Varian E-4 apparatus fitted with a Varian A-1268 variable temperature controller. Photolyses by irradiation using a Philips SP 500-W lamp. If the lamp was shut off, the spectra of **1a**-**1f** decayed within 3-6 sec. (-50°). By contrast, the sulfonyl nitroxides **2a**-**2c** are quite persistent under the same conditions.

(6) The N-bromosulfonamides were prepared from the reaction of the parent sulfonamides with *t*-BuOBr. See also: T. Ohashi, M. Okahara, and S. Komori, *Bull. Chem. Soc. Japan*, **44**, 1141 (1971) and ref. 1.

(7) Until now, we have not been able to generate **1a**-**1f** by photolysis of the corresponding N-chlorosulfonamides, the sulfonyl nitroxides being obtained instead. Since this problem

was not encountered in the photolysis of the N-bromosulfonamides in $CFCl_3$-n-pentane (1:1), we tentatively suggest that the sulfonyl nitroxides are not predominantly generated by reaction of the sulfonamidyls with traces of oxygen but by reaction with hydroperoxides. These hydroperoxides may originate via hydrogen or halogen abstraction from the solvent by Cl· followed by trapping of the carbinyl radicals by oxygen.

(8) (a) Th.A.J.W. Wajer, H.W. Geluk, J.B.F.N. Engberts, and Th.J. de Boer, Rec. Trav. Chim., **89**, 696 (1970); (b) G. Rawson and J.B.F.N. Engberts, Tetrahedron, **26**, 5653 (1970).

(9) I.I. Kandror, R.G. Gasanov, and P.K. Freidlina, Tetrahedron Lett., 1075 (1976).

(10) Coupling across the sulfonyl group has also been observed in other types of radicals; e.g. (a) C. Lagercrantz, Acta Chem. Scand., **23**, 3259 (1969); (b) E. Keller and R.G. Hayes, J. Phys. Chem., **73**, 3901 (1969).

(11) W.C. Danen and R.W. Gellert, J. Am. Chem. Soc., **94**, 6853 (1972).

(12) C. Brown and A.J. Lawson, Tetrahedron Lett., 191 (1975).

(13) Compare: P.M. Carton, B.C. Gilbert, H.A.H. Laue, R.O.C. Norman, and R.C. Sealy, J. Chem. Soc. Perkin II, 1245 (1975).