^{17}O- and ^{33}S-Hyperfine Splittings for Aromatic $\mathrm{RCO\dot{N}SAr}$ Radicals. Complete Evaluation of ESR Parameters1)

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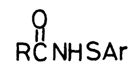
Synopsis. ^{17}O- and ^{33}S-Hyperfine splitting constants for aromatic $\mathrm{RCO\dot{N}SAr}$ radicals have been determined and the spin density distribution has been elucidated on the basis of the ESR parameters.

N-(Arylthio)acylaminyl radicals ($\mathrm{RCO\dot{N}SR'}$) have interesting structures in which both an electron-accepting (C=O) and an electron-donating substituent (SR′) attach directly to the radical center. In an earlier paper,2) we showed that in the radicals the unpaired electron resides mainly on the nitrogen and the phenylthio group on the basis of large a_N and a_H values (due to the phenylthio benzene ring protons). However, owing to a lack of the $a_{^{17}O}$ and $a_{^{33}S}$ values, we could not fully elucidate the unpaired-electron distribution pattern. We report herein the $a_{^{17}O}$ and $a_{^{33}S}$ values for the radicals.

Results and Discussion

Type-**2** radicals were generated at room temperature by the photolysis of solutions of the corresponding *N*-(arylthio)amides **1** in 1:4 (v/v) di-*t*-butyl peroxide-benzene using a 1 kW xenon lamp. Under these experimental conditions we could unequivocally detect ^{33}S-hyperfine splittings (hfs) without any enrichment of the ^{33}S atoms in each wing of the ESR spectra obtained at high gain (see Fig. 2). On the other hand, ^{17}O-hfs's could only be detected (see Fig. 1) when the radical was enriched by ^{17}O-atoms (5.9 atom%). The experimentally obtained intensity ratios of the ^{17}O (0.96%) and ^{33}S (0.20%) satellite lines to the parent peaks coincided satisfactorily with the theoretical values (^{17}O, 0.98%; ^{33}S, 0.19%), respectively. The ESR parameters obtained are listed in Table 1.


$\mathrm{R\overset{O}{\overset{\|}{C}}NHSAr}$

1


$\mathrm{R\overset{O}{\overset{\|}{C}}\dot{N}SAr}$

2

a: R=Ph, Ar=Ph ; b: R=t-Bu, Ar=C_6D_5

Type-**2** radicals can be represented by the following four possible canonical structures (A, B, C, and D) as reported in an earlier paper.2) However, the very low $a_{^{17}O}$ value obtained for **2a** reveals clearly that the canonical structure D is much less important. The π-

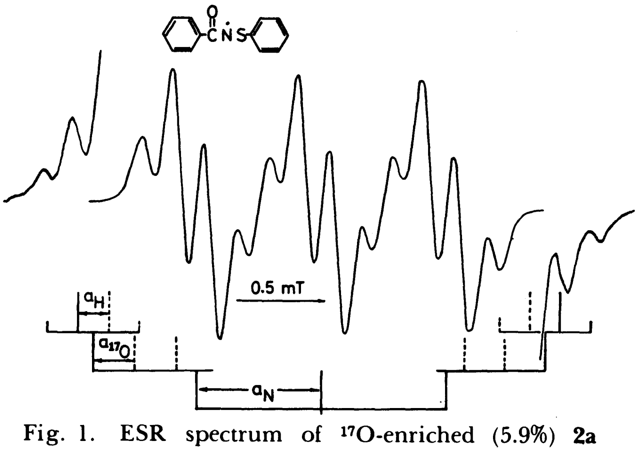


Fig. 1. ESR spectrum of ^{17}O-enriched (5.9%) **2a** recorded during photolysis of a solution of ^{17}O-enriched (5.9%) **1a** in 1:4 (v/v) di-*t*-butyl peroxide-benzene at 17 °C. The wings are shown at high gain (20 times). The stick diagram represents a part of the theoretical reconstruction of the splittings due to ^{14}N, ^{1}H, and ^{17}O. The experimentally observed satellite lines due to ^{17}O are shown by the full lines.

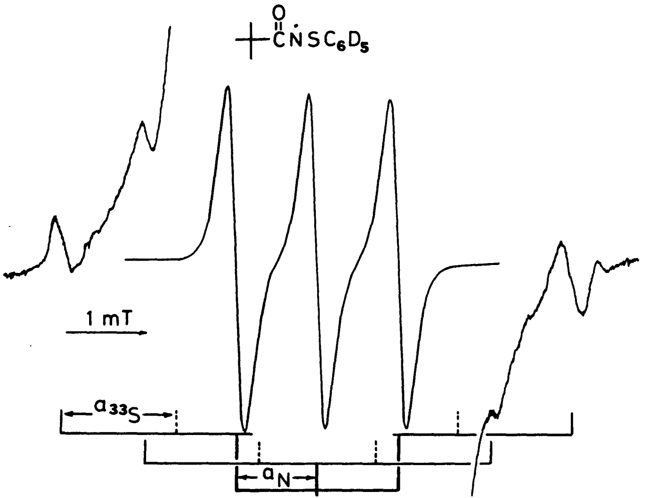
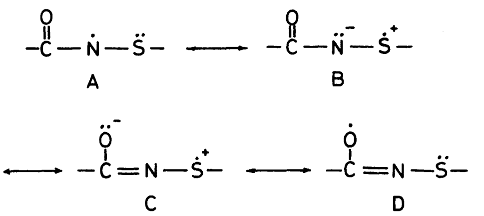


Fig. 2. ESR spectrum of **2b** recorded during photolysis of a solution of **1b** in 1:4 (v/v) di-*t*-butyl peroxide-benzene at 17 °C. The wings are shown at high gain (100 times). The stick diagram represents a part of the theoretical reconstruction of the splittings due to ^{14}N and ^{33}S. The experimentally observed satellite lines due to ^{33}S are shown by the full lines.

Table 1. ESR Parameters for Aromatic $\mathrm{RCO\dot{N}SAr}$ Radicals$^{a-c)}$

Radical	a_N	$a_H$$^{d)}$	a_{other}	g
2a	0.709$^{e)}$	0.168 (3)$^{e,f)}$	1.06 (^{33}S), 0.225 (^{17}O),$^{g)}$	2.0081$^{e)}$
2b	0.745		1.07 (^{33}S)	2.0082
t-$\mathrm{BuCO\dot{N}SPh}$	0.749$^{e)}$	0.169 (3)$^{e)}$		2.0082$^{e)}$

a) Hyperfine splitting constants are given in mT. b) Solvent 1:4 (v/v) di-*t*-butyl peroxide-benzene. c) Temperature 17±1 °C. d) Numbers in parentheses refer to the number of equivalent protons. e) Taken from Ref. 2. f) The ortho and para protons on the phenylthio benzene ring. g) The value obtained for the ^{17}O-enriched (5.9 atom%) **2a**.

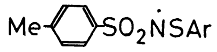


orbital spin density ($\rho_{O\pi}$) on the oxygen can be derived by using Silver's equation,[3,4] where the contribution to $a_{^{17}O}$ from $\rho_{C\pi}$ of the carbonyl carbon is neglected. The $\rho_{O\pi}$ value obtained is only 0.055.

$$\rho_O^\pi = a_{^{17}O}/Q_O = a_{^{17}O}/-4.1\ \mathrm{mT}$$

On the other hand, the $a_{^{33}S}$ values (1.06 and 1.07 mT) are much higher than the $a_{^{17}O}$ value and is strongly indicative of a high π-orbital spin density ($\rho_{S\pi}$) on the sulfur. Consequently, it can be concluded on the basis of the large a_N and $a_{^{33}S}$ values that in **2** the unpaired electron resides mainly on the nitrogen and sulfur. Accordingly, type-**2** radicals can be best represented by three canonical structures: A, B, and C.

Furthermore, we note that the $a_{^{33}S}$ values for **2** are substantially higher than those (0.46—0.74 mT) for the radicals of the type R$\dot{\mathrm{N}}$SR′ (R, R′=alkyl, aryl).[5,6] The only radical having a comparable magnitude of $a_{^{33}S}$ among the thioaminyls studied is **3**,[7] in which both an electron-accepting (SO_2) and an electron-donating substituent (SAr) attach directly to the radical center in a manner similar to **2**. The somewhat higher a_N and $a_{^{33}S}$ values for **3** can be accounted for by the fact that there is no ability of the sulfonyl group to delocalize an unpaired electron.[8]



3

$a_N = 0.79-0.894$ mT

$a_{^{33}S} = 1.19-1.23$ mT

In an earlier paper,[5] we showed that the π-orbital spin density ($\rho_{S\pi}$) on the sulfur in R$\dot{\mathrm{N}}$SR′ radicals can be derived from the $a_{^{33}S}$ values by using the following established equation through an investigation of the ^{33}S-hfs's of a variety of R$\dot{\mathrm{N}}$SR′ radicals. From

$$\rho_S^\pi = a_{^{33}S}/Q_S = a_{^{33}S}/2.3\ \mathrm{mT}$$

this equation we can estimate the $\rho_{S\pi}$ value for **2** to be 0.47. On the other hand, the $\rho_{S\pi}$ values for the R$\dot{\mathrm{N}}$SR′ radicals derived from the $a_{^{33}S}$ values of 0.46—0.74 mT are 0.20—0.32. This increased $\rho_{S\pi}$ value for **2** can be readily rationalized in terms of the contribution of canonical structure C; that is, it can be interpreted as a consequence of a synergetic effect of the electron-accepting carbonyl group and the electron-donating arylthiyl group. Therefore, we are interested in this result in connection with the hypothesis concerning captodative stabilization of radicals.[9] Further investigations are under way.

Experimental

Melting points, and IR and ^{1}H NMR spectra were taken as previously reported.[10] Benzenesulfenyl chloride,[11] deuterated benzenesulfenyl chloride,[11] and ^{17}O-enriched (5.9 atom%) benzamide[1,12] were prepared by the previously described procedures.

***N*-(Phenylthio)benzamide (1a).** This amide was prepared by the previously reported procedure,[2] with some modifications. To a solution of 200 mg (1.65 mmol) of benzamide in 15 cm^3 of dry THF was added 79 mg (2.0 mmol) of NaH (60 wt%) and the mixture was stirred for 3 h at room temperature. To this mixture was added, in one portion, at 0—5 °C with stirring a solution of 290 mg (2.0 mmol) of freshly distilled benzenesulfenyl chloride in 1 cm^3 of dry hexane. After 2 h of stirring at room temperature, 0.5 cm^3 of Et_3N was added and the resultant mixture was stirred for an aditional 0.5 h. Filtration, evaporation, column chromatography (alumina, Merck Art 1097, column size 3×10 cm, 1:100 ethanol–benzene), and crystallization (benzene–hexane) gave **1a** in 67% yield (260 mg, 1.1 mmol); mp 123—124 °C (lit,[2] 122—124 °C).

^{17}O-Enriched **1a** was prepared by the same method; mp 123—123.5 °C.

***N*-(Phenylthio-d_5)pivalamide (1b).** To a stirred solution of 2.02 g (20 mmol) of pivalamide and 4 cm^3 of Et_3N in 300 cm^3 of dry ether was added dropwise at 0—5 °C a solution of 3.59 g (24 mmol) of benzenesulfenyl-d_5 chloride in 20 cm^3 of dry ether. After being stirred for 3 h at the same temperature, the mixture was filtered, evaporated, and chromatographed as described above. Crystallization from hexane gave colorless needles in 21% yield (0.91 g, 0.42 mmol); mp 98—99 °C; IR (KBr) 3250 (NH), 1670 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.16 (s, *t*-Bu, 9H), 7.91 (s, NH, 1H). Anal. ($C_{11}H_{10}D_5NOS$) C, H, N.

ESR Measurements. A 10—20 mg portion of amide **1** and 0.40 cm^3 of 1:4 (v/v) di-*t*-butyl peroxide–benzene were placed in an ESR cell. The cell was then degassed by three freeze-pump-thaw cycles using a high-vacuum system and sealed off. Type-**2** radicals were generated in the cavity of an ESR instrument by direct irradiation using a 1-kW xenon lamp (Wacom UV-10X). The ESR spectra were recorded during irradiation on a JEOL JES-FE-2XG spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. Hyperfine-splitting constants and *g* values were determined by a comparison with Fremy's salt in K_2CO_3 aqueous solution (a_N=1.309 mT, g=2.0057).

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