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Spin Trapping of Thiocyanatyl ($^{\bullet}$SCN) Radicals by Nitrone Spin Traps

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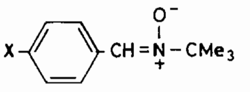
Although spin trapping using nitrone spin traps has been proven to be a suitable method for the detection of halide atoms and pseudohalide radicals such as $^{\bullet}$CN, $^{\bullet}$NCO and $^{\bullet}N_3$ in solution [1–5], attempts to detect thiocyanatyl radicals ($^{\bullet}$SCN) generated by electrochemical oxidation of SCN^- have failed [1]. On the other hand, spin trapping experiments with nitromethane acid-anion have provided evidence for the formation of $^{\bullet}$SCN radicals during the oxidation of SCN^- by hydroxyl radicals [6]. However, this spin trap requires a higher pH which limits its application range. Moreover, no evidence for the formation of $(SCN)_2^{\bullet-}$ radicals was obtained with this spin trap.

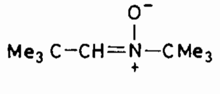
In order to find a reliable method for the detection of both $^{\bullet}$SCN and $(SCN)_2^{\bullet-}$ radicals, we have studied the reaction of these radicals with various nitrone spin traps in acetonitrile solutions.

Thiocyanatyl radicals were generated by photochemical one-electron oxidation tetrabutylammonium thiocyanate in the presence of chloranil (330 nm < λ < 600 nm). Similar results were obtained with $CBrCl_3$ as a photooxidizing agent. In this case, however, the ESR spectra were superimposed by the signals of the CCl_3 spin adduct. Phenyl-*N*-tert-butyl nitrone (PBN), 4-chlorophenyl-*N*-tert-butyl nitrone (4-ClPBN), 5,5-dimethylpyrroline-1-oxide (DMPO), and di(tert-butyl)nitrone (DBN) were used as spin traps.



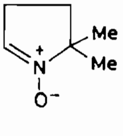
X = H PBN

X = Cl 4-ClPBN



$$Me_3C{-}CH{=}\overset{\overset{\textstyle O^-}{|}}{\underset{+}{N}}{-}CMe_3$$

DBN



DMPO

TABLE I. Hyperfine Coupling Constants[a] of Spin Adducts Formed by Spin Trapping of $^{\bullet}$SCN and $(SCN)_2^{\bullet-}$ radicals

Spin trap	$^{\bullet}$SCN adduct		$(SCN)_2^{\bullet-}$ adduct		
	a_N	a_H	$a_N{}^1$	$a_N{}^2$	a_H
DBN	1.424		1.478	0.392	
PBN	not observed[b]		1.444	0.386	0.109
4-ClPBN	not observed		1.433	0.368	0.109
DMPO[c]	1.29	1.11	1.33	0.20	1.92

[a] All coupling constants given in mT ±0.005 mT. [b] An unidentified nitroxide (see text) was observed. [c] Coupling constants ±0.02 mT.

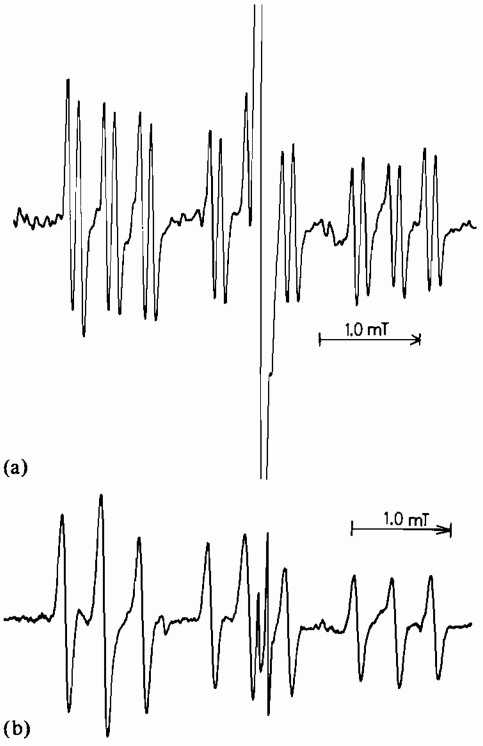


Fig. 1. ESR signals of the spin adducts obtained by $(SCN)_2^{\bullet-}$ radical addition to (a) PBN, and (b) DBN, respectively.

The photolysis of chloranil/SCN^- in the presence of these spin traps led to readily detectable nitroxides (Table I). Typical ESR spectra of nitroxides formed upon photolysis of tetrabutylammonium thiocyanate (0.01 M) and chloranil (0.005 M) in the presence of 0.02 M PBN and DBN, respectively, are shown in Fig. 1. The hyperfine splitting of the ESR signals suggests the trapping of a nitrogen-centered radical. Since it is known [7] that $^{\bullet}$SCN radicals react with SCN^-, eqn. (1), we have assigned these signals to the $(SCN)_2^{\bullet-}$ spin adducts.

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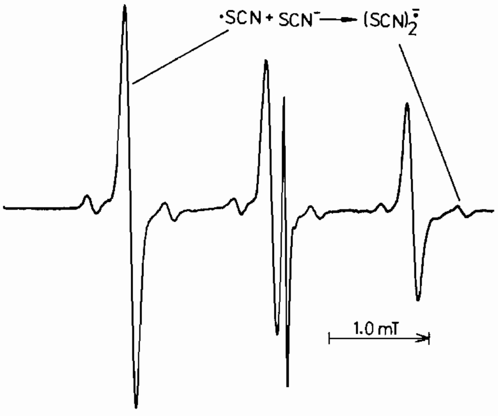

Fig. 2. ESR spectra of the nitroxides formed by spin trapping of $^{\bullet}SCN$ and $(SCN)_2^{\bullet-}$ by DBN (photolysis of acetonitrile solution of chloranil (0.0049 M), tetrabutylammonium thiocyanate (0.0133 M), and DBN (0.37 M) at 295 K under anaerobic conditions).

$$^{\bullet}SCN + SCN^- \longrightarrow (SCN)_2^{\bullet-} \qquad (1)$$

$(k_1 = 6.8 \times 10^9\ M^{-1}\ s^{-1}$ [7])

The assignment is further supported by the results obtained by alteration of the concentrations of the thiocyanate and the spin trap, respectively. Thus, the increase of the spin trap concentration and/or the decrease of the concentration of the thiocyanate led to the appearance of a new ESR signal which is displayed for DBN in Fig. 2. Both the hyperfine splitting (lack of secondary ^{14}N-splitting) and the slight increase of the g-value ($\Delta g = 0.0003$) are in agreement with the trapping of a S-centered radical. Hence, the latter nitroxide is assigned to the spin adduct of the $^{\bullet}SCN$ radical.

Using the rate constant for the reaction (1), a rough estimation of the rate constant for the spin trapping reaction of $^{\bullet}SCN$ radicals by DBN ($k = (1.6 \pm 0.7)\ 10^9\ M^{-1}\ s^{-1}$) may be made from the relative ESR intensities of the $^{\bullet}SCN$ and $(SCN)_2^{\bullet-}$ spin adducts at given concentrations of SCN^- and DBN, respectively. Although the low stability of the $^{\bullet}SCN$ and $(SCN)_2^{\bullet-}$ spin adducts (lifetime $\lesssim 5$ s) rules out an accurate determination of the spin trapping rate constant from stationary ESR experiments, the relative ESR intensities of the spin adducts of DMPO suggest a value of the same order of magnitude as obtained for DBN. On the other hand, spin trapping of $^{\bullet}SCN$ radicals by PBN (and 4-ClPBN) hardly competes with the addition to SCN^-. Although the structure of the nitroxide formed at high PBN concentration ($c_{PBN}/c_{SCN^-} > 100$) is not known, the hyperfine structure of the ESR signal ($a_N^1 = 1.260$ mT, $a_N^2 = 0.613$ mT, $a_H^1 = 0.613$ mT, $a_H^2 = 0.050$ mT) rules out an addition of the $^{\bullet}SCN$ radical to the nitrone double bond.

Summarizing, spin trapping with DBN may be recommended for the ESR detection of both $^{\bullet}SCN$ and $(SCN)_2^{\bullet-}$ radicals in liquid solution at ambient temperature.

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