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EPR Studies on Carboxylic Esters. Part 14.[1] Radical Anions of *O*-Phenyl Halobenzenecarbothioates†‡

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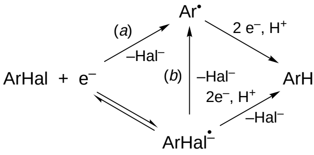
Radical anions of *O*-phenyl halobenzenecarbothioates are generated by *in situ* electroreduction and shown to be mostly persistent by their EPR spectra; in certain cases, dependent on the nature and position of the halogen substituent, elimination of halide anions occurs.

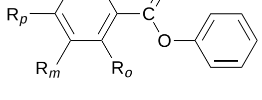
Radical anions of arenes with electron-withdrawing substituents such as nitro, carbonyl, alkoxycarbonyl (ester) or the corresponding thiocarbonyl groups are readily formed by chemical or electrochemical single electron transfer (SET). They are usually persistent species and their EPR spectra have been studied extensively.[1,2] Radical anions of halobenzenes are, however, extremely labile if they exist at all. In general, according to Scheme 1, halide ions are eliminated simultaneously with (*a*) or immediately after (*b*) the SET process. Even in the latter case EPR detection of the primary radical anion $ArHal^{\bullet-}$ is hardly possible. As a result the radical anion $ArH^{\bullet-}$ of the protiodehalogenated arene is observed.



Scheme 1

This array of reactions has been studied by electrochemical and related experimental methods[3] as well as by quantum chemical calculations.[4] Whereas the stabilizing effect of a nitro substituent is strong enough to keep *meta*-chloro- and *meta*-bromo-nitrobenzene radical anions intact, immediate elimination of iodide occurs from *meta*-iodonitrobenzene.[5] The radical anions of the chlorobenzaldehydes,[6] chloroacetophenones,[7] chlorobenzonitriles[8] and methyl chlorobenzoates,[4c] on the other hand, are too short-lived even at low temperatures to be detectable by EPR spectroscopy.

We therefore studied the radical anions of *O*-phenyl halobenzenecarbothioates **1–4** since the strong electron-withdrawing effect and the high polarizability of the thiocarbonyl group[9] should give rise to a pronounced stabilization of the radical anions.



1–6
(*cf.* Table 1 for R$_o$, R$_m$, R$_p$)

Results and Discussion

The radical anions $\mathbf{1}^{\bullet-}$–$\mathbf{6}^{\bullet-}$ were generated by *in situ* electroreduction in dry DMF as described previously.[1,9,10] Intense and well resolved EPR spectra were recorded, Fig. 1. The experimental data, *i.e.* the proton and fluorine hfs coupling constants, are shown in Table 1.

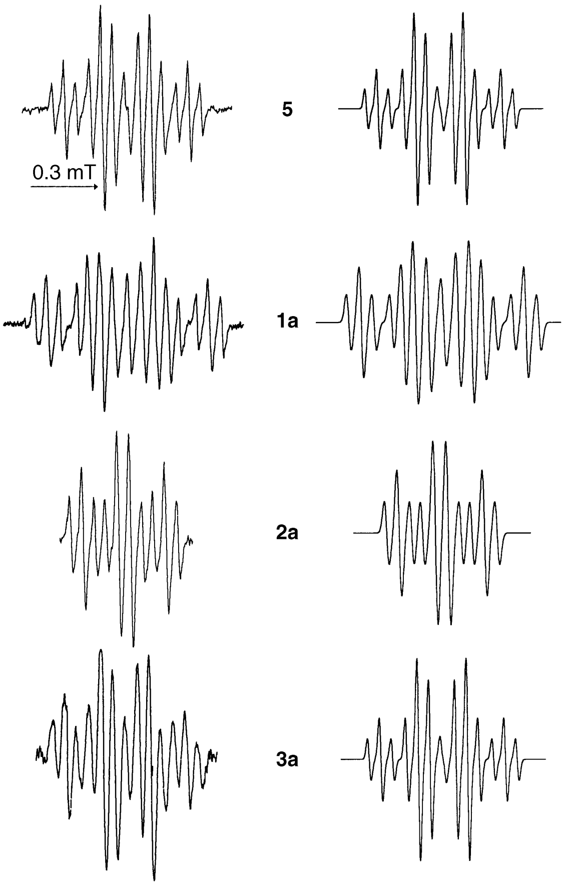


Fig. 1 Experimental (left) and simulated (right) EPR spectra of the radical anions obtained from *O*-phenyl thiobenzoate (**5**), 2-fluorothiobenzoate (**1a**), 2-chlorothiobenzoate (**2a**) and 2-bromothiobenzoate (**3a**)

Inspection and consideration of the results allows a clear and consistent conclusion to be drawn. Obviously the stability of the thiono ester radical anions is controlled by the nature of the halogen substituent and its position in the benzene ring. All the isomeric fluoro **1** and chloro **2** derivatives are persistent. By comparison with the unsubstituted **5** and *para-tert*-butyl **6** thiono benzoate it is possible to assign the ^{1}H and also the ^{19}F coupling constants. The latter are larger by a factor of *ca.* 2 as compared with the former if equivalent positions are considered. This effect is known from the literature.[2a] Owing to the very small hfs coupling constants no splitting of the chlorine nuclei was observed. Therefore, one splitting is missing in $\mathbf{2a}^{\bullet-}$, $\mathbf{2b}^{\bullet-}$ and $\mathbf{2c}^{\bullet-}$ and as a consequence the EPR spectrum of $\mathbf{2c}^{\bullet-}$ is nearly identical with that of $\mathbf{6}^{\bullet-}$. Only the EPR spectrum of the *meta*-isomer $\mathbf{3b}^{\bullet-}$ can be observed in the bromothiono ester series **3**. In this case the

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1997, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

‡Dedicated to Professor Hans Schäfer on the occasion of his 60th birthday.

Table 1 Hfs coupling constants a in *O*-phenyl arenecarbothioate radical anions $\mathbf{1}^{\bullet-}$–$\mathbf{6}^{\bullet-}$

	Substituents			Coupling constants, mT				
Compound	R_o	R_m	R_p	a_2	a_3	a_4	a_5	a_6
1a	F	H	H	0.670	0.125	0.520	0.125	0.425
1b	H	F	H	0.363	0.250	0.580	0.104	0.320
1c	H	H	F	0.396	0.129	1.025	0.129	0.396
2a	Cl	H	H	—	0.125	0.483	0.125	0.358
2b	H	Cl	H	0.363	—	0.592	0.107	0.242
2c	H	H	Cl	0.380	0.122	—	0.122	0.380
3a	Br	H	H		EPR spectrum of $\mathbf{5}^{\bullet-}$, *cf.* text			
3b	H	Br	H	0.367	—	0.479	0.108	0.367
3c	H	H	Br		EPR spectrum of $\mathbf{5}^{\bullet-}$, *cf.* text			
4	H	I	H		EPR spectrum of $\mathbf{5}^{\bullet-}$, *cf.* text			
5	H	H	H	0.375	0.117	0.483	0.117	0.375
6	H	H	Bu^t	0.367	0.122	—	0.122	0.367

3-position appears as a blind spot. As for the rest the coupling constants of $\mathbf{3b}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$ are nearly identical. The radical anions of the *ortho*- $\mathbf{3a}^{\bullet-}$ and *para*-bromo thiono ester $\mathbf{3c}^{\bullet-}$ cannot be detected. The spectrum of $\mathbf{5}^{\bullet-}$ is instead observed. The same is true for the *meta*-iodo derivative **4**. The protons needed for the protiodehalogenation obviously originate from traces of water or Hofmann elimination of the quaternary ammonium salt used as the supporting electrolyte.

This result is not quite unexpected. It can be explained by the weakness of the carbon–bromine and carbon–iodine bonds as compared to the carbon–fluorine and carbon–chlorine bonds. It is, however, not in agreement with the enhanced reactivity of activated fluoroarenes in aromatic nucleophilic substitution (S_NAr) reactions. In this case the attack of the nucleophile is the rate-determining step. It is controlled by the electron density at the respective carbon centre, which is the lowest if fluorine is the substituent. The leaving group ability is therefore irrelevant.[11] With radical anions, on the contrary, the latter is the determining step since the 'nucleophilic attack', *i.e.* the SET process, is fast in any case.

The regioselectivity observed in the bromo series $\mathbf{3}^{\bullet-}$ can be explained qualitatively by the spin densities, which are proportional to the proton hfs coupling constants. Accordingly, the elimination of bromide from the *ortho*- and *para*-position is fast, whereas the *meta*-derivative $\mathbf{3b}^{\bullet-}$ is long-lived enough to be detected spectroscopically by EPR.

It is noteworthy that the spin density distribution in the *O*-phenyl halobenzenecarbothioate radical anions $\mathbf{1}^{\bullet-}$–$\mathbf{3}^{\bullet-}$ is determined by the phenoxythiocarbonyl substituent and is hardly influenced by the halogen substituents.

Experimental

The *O*-phenyl arenecarbothioates **1–6** were prepared by thionation of the corresponding esters with Lawesson's reagent in chlorobenzene as described in the literature.[12] The radical anions were generated by *in situ* electroreduction at the appropriate reduction potentials.[12] A solution containing 10^{-3} mol l^{-1} **1–6** and 0.1 mol l^{-1} of tetrapropylammonium bromide in dry DMF was used as the supporting electrolytic solvent and a silver wire was used as the internal reference electrode. The EPR spectra were recorded at room temperature on a Bruker 420 S spectrometer (X-band).[1,9,10]

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