ESR Studies on Carboxylic Esters

Part 13[†]—Electron Spin Resonance Spectroscopy and Molecular Orbital Calculations on the Radical Anions of 2-Oxo-carbothioate and 2-Oxo-carbodithioate Esters

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Radical anions of alkyl α -oxocarbothioates and α -oxocarbodithioates are generated by *in situ* electroreduction. Their spin density distribution and configuration are discussed in terms of the ESR spectra and semi-empirical (McLachlan-type and AM1) MO calculations.

KEY WORDS ESR *a*-Oxo-carbothioates *a*-Oxo-carbodithioates Radical anions MO calculations

INTRODUCTION

Alkyl phenylglyoxalates (1) are easily transformed into persistent radical anions by electron transfer. Their ESR spectra clearly show an extensive spin delocalization over the whole molecule.² On preparative electroreduction in protic³ as well as in aprotic⁴ media, 1 is reduced at its keto rather than its ester group. Reduction of methyl 1,1-dithiophenylglyoxalate (4a), on the other head, exclusively occurs at its thiocarbonyl group.⁵ This corresponds to the observation that the radical anions of O-alkyl carbothioate and alkyl carbodithioate esters accumulate much more spin density in their functional groups than the radical anions of alkyl carboxylates do⁶ and that the spin density is considerably higher in the thioester group if both functionalities are present in one molecule.⁷ Despite the higher electronegativity of oxygen as compared with sulphur this is not unexpected since sulphur and, in particular, thiocarbonyl sulphur exhibits the higher polarizability. Accordingly, the same effect has been clearly demonstrated in the monothio-1,2-diketone series by experimental and theoretical methods.8

RESULTS AND DISCUSSION

2-Oxo-thiono-⁹ and 2-oxo-dithiocarboxylic esters^{10,11} have become easily available. We have, therefore, undertaken a systematic electrochemical and ESR investigation on the radical anions of 1–7 in order to compare the spin density distribution in compounds of the general type R¹-CO-CX-YR² (X, Y = O, S) with each other as well as with the corresponding amides (Y = NR) and thioketones R¹-CS-CX-YR².^{13,14} We will report elsewhere about radical anions of phenylglyoxy-

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lic amides, thioamides, 2-thioxocarboxylic esters and thioesters. We have already mentioned the radical anions $3d^{-1}$, $4b^{-1}$ and $4c^{-1}$ in Part 11 of this series.¹⁵

Electrochemistry and ESR spectroscopy

The thioesters 2-4 of phenylglyoxylic acid exhibit a polarographic one-electron reduction step in aprotic medium, which is reversible according to the cyclovoltamogram. The half-wave potential is shifted in the positive direction if sulphur is introduced into the ester molecule (cf. Table 1). This effect is also observed in the benzoate ester series.⁷ There is, however, an additional shift to more positive values in the half-wave potentials of the phenylglyoxalates as compared with the corresponding benzoates (Table 1). The electron transfer is facilitated by the presence of the α -keto group, which allows a more pronounced electron delocalization to

Table 1. Polarographic half-wave potentials $E_{1/2}$ (V vs. SCE) of alkyl phenylglyoxalates, benzoates and their sulphur derivatives							
		Ph-CO-	CX-YEt	Ph-CX-YMe ⁷			
х	Y	$E_{1/2}(1)$	$E_{1/2}(2)$	$E_{1/2}(1)$	$E_{1/2}(2)$		
0	0	-1.48 ²		-2.24			
0	S	-0.98	-1.91	-2.00	-2.50		
S	0	-0.99	-1.87	-1.60	-2.11		
S	S	-0.81	-1.47	-1.32	-1.90		

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Nr.	R'	R ²	R³	a ^H ortho	a ^H meta	a ^H para	a ^H R1	g factor
1aª	Me	н	н	0.246	0.083	0.280	0.083	
1ь	Et	н	tBu	0.246	0.083		0.083	2.004 89
2a ¹³	Me	Ή	н	0.182	0.059	0.275	0.059	2.00513
2b ⁵	Me	н	tBu	0.180	0.060		0.060	2.005 22
2c	Et	н	Н	0.180	0.060	0.258	0.032	2.005 33
2d	iPr	н	н	0.183	0.059	0.243	0.030	2.005 31
2e	tBu	н	н	0.181	0.058	0.213	—	2.005 36
2f	Ph	н	н	0.172	0.057	0.200		2.005 02
3a	Me	н	н	0.060	0.030	0.074	0.174	2.008 09
3b°	Me	tBu	н	0.057	_	0.071	0.176	2.008 04
3c	Me	н	tBu	0.058	0.029		0.167	2.008 47
3d	Et	н	tBu	0.060	0.030		0.180	2.008 09
4a	Me	н	н				0.167	2.011 08
4b	Me	tBu	Н	0.045		0.049	0.149	2.011 08
4c ^d	Me	н	tBu	0.047	0.028		0.152	2.011 05
4d	Me	н	OMe	0.052	0.030		0.158	2.01093
4e	Et	н	н					2.011 04
4f	Et	tBu	н	0.0455	—	0.0439	0.0903	2.011 07
4g	iPr	н	н					2.011 03
4h	iPr	tBu	Н	0.0455		0.0433	0.0499	2.011 05
4i	tBu	н	н				_	2.011 57
4j	PhCH₂	н	н	0.050		0.050	0.065	2.01099
5	Me				e		0.114	2.004 72
6 ^r	Me						0.186	2.007 76
7a ⁹	Me						0.159	2.01048
7b ^Ւ	Æt						0.101	2.010 38

Table 2. Hyperfine coupling constants a^{H} (mT) and g factors of the radical anions 1-•_7

^a In agreement with Ref. 2.

^b 2b was not isolated. The ESR spectrum of 2b⁻⁺ appeared simultaneously with the spectrum of its isomer 3c-1

^ca^c(CS) = 0.678 mT. $^{d}a^{c}(CS) = 1.056 \text{ mT}.$ ^ea^H(tBu) = 0.038 mT (9 H). $a^{c}(CS) = 1.027 \text{ mT}.$ ⁹ a^c(CS) = 1.156 mT. ^ha^c(CS) = 1.196 mT.

occur. As shown in Table 1, a second electron can be transferred at more negative potentials under formation of a dianion.

The radical anions of 1-7 were generated by in situ electroreduction at the potential of the first polarographic wave and their ESR spectra were measured at room temperature in solution. The experimental hyperfine coupling constants and g factors are compiled in Table 2. Assignment of the coupling constants to the various protons was possible and in most cases unequivocal through comparison of the derivatives with tert-butyl substituents in specific ring positions or with differing alkyl substituents in the ester groups. Even the radical anions 5^{-1} of esters and thioesters derived from the aliphatic 3,3-dimethyl-2-oxobutanoic acid ('trimethylpyruvic acid') are persistent enough to give ESR spectra (Table 2).

The ESR spectra of the dithioester radical anions 4⁻⁻ are not well resolved since the coupling constants of the aryl protons are particularly small and in some cases (4a, e, g, i) not measurable at all. Exchange of ring protons for tert-butyl groups significantly improves the resolution. Accordingly, the coupling constants of tertbutyl derivatives can be determined by simulation. This may be seen in Fig. 1 (1b^{-•}), Fig. 2 (3d^{-•}) and Fig. 3 (4c^{-•}). The small coupling constants of $4^{-•}$ are indica-



Figure 1. ESR spectrum of 1b⁻⁺ (left) with simulation (right).

tive of a low spin density ρ_{ar}^{π} in the aromatic ring and, consequently, a relatively high spin density $\rho_{\rm f}^{\pi}$ in the functional group. Taking McConnell's relation ρ_{ar}^{π} = $a_{ar}^{\rm H}/Q$ as a basis the following sequence is found:

$$\rho_{\rm ar}^{\pi}(1) > \rho_{\rm ar}^{\pi}(2) > \rho_{\rm ar}^{\pi}(3) > \rho_{\rm ar}^{\pi}(4)$$







Figure 3. ESR spectrum of 4c⁻⁺ (left) with simulation (right).

and, considering the methyl proton coupling constants

$$\rho_{f}^{\pi}(\text{COCO}_{2}\text{Me}) < \rho_{f}^{\pi}(\text{COCOSMe})$$
$$< \rho_{f}^{\pi}(\text{COCSOMe})$$
$$< \rho_{f}^{\pi}(\text{COCS}_{2}\text{Me}).$$

In fact the ESR-spectra of the thiono ester radical anions 3^{-} are better resolved (cf. Fig. 2) and the corresponding ring proton coupling constants higher as compared with 4^{-} .

The same trend is reflected in the g factors which can be correlated with the spin densities at heavy atoms (sulphur):

$$g(\text{COCO}_2 \text{R}) < g(\text{COCOSR})$$

 $< g(\text{COCSOR})$
 $< g(\text{COCS}_2 \text{R}).$

These findings correspond to the above mentioned results from related series of compounds with carbonyl and more polarizable thiocarbonyl groups. They also agree with the fact that ¹³C satellite lines of the thiocarbonyl carbon atoms at natural abundance are observed in the ESR spectra of $3b^{-*}$ and $4c^{-*}$ (Table 2). Due to the high spin density the ¹³C hyperfine coupling constants are large enough to make the weak satellite lines close to the wings of the main lines visible. This effect is even more pronounced in the aliphatic derivatives 6^{-*} and 7^{-*} in which the spin density is completely localized in the functional group.

As shown in Table 2 the respective two ortho and meta protons in the aromatic radical anions are equivalent. This is referred to fast rotation of the benzene ring about the C_{ar} —CO bond on the ESR time scale. It is also observed in benzoate ester and thiobenzoate ester radical anions,⁶ but not, however, in the related amides and thioamides.¹⁶

Table 3. Calculated (AM1) and experimental (4a, x-ray) bond lengths d (pm), angles α (°) and torsion angles τ (°) in 1a (X=Y=O), 2a (X=O, Y=S), 3a (X=S, Y=O) and 4a (X=Y=S) and the corresponding radical anions

\dot{c}_4 \dot{c}_2 \dot{c}_2 \dot{c}_2									
	1a	1a	2a	2a	За	3a-'	4a*	4 a	4 a
d(C1-C7)	147.0	142.0	147.3	142.2	147.2	149.8	149.2	147.7	150.6
d(C7-0)	123.1	125.8	123.2	126.3	123.3	125.4	119.9	123.4	123.7
d(C7-C8)	151.1	151.2	151.4	150.5	151.3	143.9	152.6	150.3	145.9
d(C8-X)	123.1	123.3	123.5	123.2	154.9	161.4	162.1	154.4	160.7
d(C8-Y)	136.3	137.9	171.1	175.7	136.7	140.7	170.9	166.8	169.9
d(C9-Y)	143.0	141.8	175.4	175.3	143.0	141.6	179.9	174.6	175.5
α(C1-C7-O)	124.5	127.2	123.7	126.2	123.6	117.2	123.7	122.6	118.4
α(C1-C7-C8)	115.8	116.0	115.8	116.5	116.7	118.7	117.8	116.2	115.8
α(C7-C8-X)	128.1	130.7	121.5	126.1	123.8	126.8	118.4	120.9	118.6
α(C7-C8-Y)	112.7	113.4	111.3	110.5	107.9	111.4	112.9	109.1	113.4
α(C8-Y-C9)	116.7	117.0	104.6	105.1	116.4	114.8	103.2	105.1	103.4
τ(C2-C1-C7-C8)	15.1	-0.4	154.0	178.4	2.9	48.8	-21.7	-35.2	-35.9
τ(C1-C7-C8-X)	-76.1	-78.9	83.8	86.1	~103.8	-178.3	-69.4	83.9	80.8
τ(C9-Y-C8-X)	1.7	-1.3	0.6	1.4	-2.7	-5.7	2.1	0.1	0.7
^a Data from the x-ray analysis. ¹⁹									

Molecular orbital calculations

We have performed semi-empirical MO calculations on the prototype compounds 1a-4a and their radical anions using the AM1 method.¹⁷ Bond lengths and angles of the neutral molecules were found to agree well with experimental values for ordinary esters and thioesters.¹⁸ Since an x-ray structural analysis of 4a has been published¹⁹ a direct comparison of the calculated and experimental values is possible for the α -oxodithioester (cf. Table 3). It turns out that the calculated C-S bond lengths are found to be too short. This seems to be a general feature of currently used MO calculation programs since we have found the same deviations for thioketones.⁸ Furthermore, the calculated torsion angles between the planes of the benzene ring and the carbonyl group as well as the carbonyl and the thiocarbonyl group are too large. Apparently, at least in the crystalline state, the 4a molecules are actually less twisted than theoretically predicted. No experimental data are available for the α -oxo-ester 1a and the α -oxo-thioloester 2a. These two compounds can, however, be comwith a related α -diketone, 1-phenyl-1,2pared propanedione, which exhibits torsion angles of 10° between the phenyl and carbonyl group and 130° between the two carbonyl groups²⁰—in fair agreement with our calculations (cf. Table 3).

According to our calculations the geometries of the radical anions are significantly different from those of the corresponding neutral molecules. In both 'carbonyl' esters, 1a and 2a, the bonds between the benzene ring and the keto group are shortened and the keto-carbonyl groups themselves are elongated upon electron uptake and formation of the radical anions. In addition, a coplanar arrangement of the phenyl and carbonyl group is achieved. Both effects can be taken as indicative of a preferred localization of spin density in the benzoyl group. On the other hand, in both 'thiocarbonyl' esters, 3a and 4a, the bonds between the benzene ring and the carbonyl group as well as the carbon sulphur double bonds are longer in the radical anions whereas the bonds between the carbonyl and the thiocarbonyl group are shorter. The torsion angle between the plane of the ring and the carbonyl group is increased in the thiono ester radical anion 3a^{-*}. Correspondingly, a planar conformation of the central α -oxothiono ester moiety is achieved. No significant changes in the conformation of the dithio ester 4a and its radical anion 4a^{-•} occur.

Spin densities as determined from McLachlan and AM1¹⁷ calculations are given in Table 4 together with values which were obtained from experimental proton coupling constants using McConnell's equation, $a_{\mu}^{H} = -2.2\rho_{\mu}^{\pi}$. McLachlan-type calculations on the ester and thiolester radical anions $1a^{-1}$ and 2^{-1} expectedly create spin densities ρ_{μ}^{π} that are in good agreement with the experimental values. The AM1 calculations including configurational interaction (CI) also yield results which are acceptable for $1a^{-1}$ and $2a^{-1}$. In particular, the higher spin densities in the *para* positions as compared with the *ortho* positions are correctly reproduced whereas the McLachlan calculations in contradiction to the unequivocal experimental results.

Table 4. Spin density distribution in the benzene ring of the radical anions 1a⁻⁻-4a⁻⁻

Nr.	Pos. µ	<i>а^нµ</i> (mT)	ρ,*=a, ^H /2.2	ρ"* (McL)*	ρ,* (AM1)
1a	2	0.246	0.112	0.1115	0.1381
	3	0.083	0.038	-0.0384	0.0153
	4	0.280	0.127	0.1015	0.2136
	5	0.083	0.038	-0.0384	0.0244
	6	0.246	0.112	0.1115	0.1122
2a	2	0.182	0.083	0.0995	0.0995
	3	0.059	0.027	-0.0406	0.0202
	4	0.275	0.125	0.0909	0.1836
	5	0.059	0.027	-0.0406	0.0134
	6	0.182	0.083	0.0995	0.1162
3a	2	0.060	0.027	0.1205	0.0160
	3	0.030	0.014	-0.0474	0.0044
	4	0.074	0.034	0.1111	0.0251
	5	0.030	0.014	-0.0474	0.0034
	6	0.060	0.027	0.1205	0.0163
4a	2	0.045	0.020	0.1102	0.0146
	3	0.028	0.013	0.0438	0.0104
	4	0.049	0.022	0.1018	0.0349
	5	0.028	0.013	0.0438	0.0041
	6	0.045	0.020	0.1102	0.0197
^a McL	.achlan ca	alculations,	l = 1.2.		

As mentioned above the thiono $(3a^{-1})$ and to an even greater extent the dithio ester radical anions $4a^{-1}$, exhibit low spin densities in the aromatic rings and, correspondingly, high overall spin densities in the functional groups. This effect is well reproduced by the AM1 calculations (cf. Table 4) and is demonstrated in Fig. 4. The calculated spin densities of each of the two chemically equivalent ortho (2,6) and meta (3,5) positions are different, whereas the corresponding experimental proton coupling constants are equal within experimental error in all cases (cf. Table 2). This should be due to internal rotation of the benzene ring, which is fast on the ESR time scale at room temperature.

Aromatic spin densities far too high result from McLachlan calculations (Table 4) which imply an unrealistic, fixed coplanar structure with perfect π -electron delocalization over the whole molecule.

EXPERIMENTAL

Spectra

IR Spectra: Perkin–Elmer 297 and 399. UV–VIS Spectra (methanol): Perkin–Elmer 200. NMR Spectra ($CDCl_3$, TMS as internal standard) were recorded on Varian T60, Bruker WH270, EM400 and WP60 (¹³C) spectrometers.

ESR Spectra were obtained on a Bruker 420s spectrometer (X-band) equipped with a Bruker gaussmeter







Figure 4. SOMO electron densities of $1a^{-}-4a^{-}$ in a plane 70 pm above the benzene ring (AM1 calculations). In case of the



thiono and dithioesters $3a^{-}$ and $4a^{-}$ the functional groups are considerably twisted out of the plane.

and a microwave counter as described earlier.^{16,21} The generation of radical anions by *in situ* electroreduction in dry DMF at room temperature has been described elsewhere.^{16,21} AM1 calculations¹⁷ were performed on a RISC 6000 workstation. Configurational interaction was considered for the radical anions. Fixed values of the C—H bond lengths and C—C—H bond angles as obtained for the neutral molecules were used for the radical anions in order to save computation time; all other geometric parameters were optimized.

Compounds

Methyl 2-oxo-2-phenylethanoate (1a) was a commercial sample. O-Methyl 2-oxo-2-phenylethanethioate (3a),⁹ S-methyl 2-oxo-2-phenylethanethioate (2c),²³ S-phenyl 2-oxo-2-phenylethanethioate (2f),²⁴ O-methyl-2-(3,5-di-*tert*-

butylphenyl)-2-oxoethanethioate (3b),⁹ O-methyl 2-(4-tert-butylphenyl)-2-oxoethanethioate (3c),⁹ methyl 2-oxo-2-phenylethanedithioate (4a),¹¹ methyl 2-(4-methoxyphenyl)-2-oxoethanedithioate (4d),¹¹ O-methyl 3,3-dimethyl-2-oxobutanethioate (6),⁹ methyl 3,3dimethyl-2-oxobutanedithioate (7a),¹¹ and ethyl 3,3-dimethyl-2-oxobutanedithioate $(7b)^{11}$ are described in the literature. The following are novel compounds; their characteristic data are compiled in Table 5.

Ethyl 2-(4-*tert*-butylphenyl)-2-oxoethanoate (1b) was obtained by oxidation of ethyl 4-(*tert*-butylphenyl)acetate^{25,26} with CrO_3 in boiling acetic acid.

S-Isopropyl (2d) and S-tert-butyl (2e) 2-oxo-2-phenylethanethioate were obtained from phenylglyoxylic chloride²⁷ and the corresponding alkanethiol in diethyl ether in the presence of triethylamine.

O-Ethyl 2-(4-tert-butylphenyl)-2-oxoethanethioate (3d) was obtained analogously to 3c.⁹

Alkyl 2-aryl-2-oxoethanedithioates (4) were prepared from 1-aryl-2bromoethanones (obtained by bromination of the corresponding acetophenones with Br_2 in acetic acid at 70 °C) and S_8 (3 equ.) in DMF in the presence of triethylamine (3 equ.) as described by Mayer *et al.*¹⁰

Methyl 3,3-dimethyl-2-oxobutanoate (5) was prepared by oxidative desulfurization of 6 with Hg(OAc)₂ in acetic acid at room temperature.

Table 5. Experimental and spectroscopic data of novel a-oxo-carboxylic esters and thioesters^a

1b 19 90–94/0.05 1710 1.32 (s, tBu); 1.40 (t, CH ₃); 4.44 (q, OCH ₂); 1680 7.51 (d, 2ArH); 7.95 (d, 2ArH)	
2d 75 103–104/0.3 1670 1.03 (d, 2CH ₃); 3.74 (sept, SCHMe ₂); 7.70 (m, 5ArH)	
2e 57 29–30 (hexane) 1675 1.58 (s. tBu): 7.74 (m. 5ArH)	
3d 30 128–129/0.1 1670 1.34 (s, tBu); 1.51 (t, CH ₃); 4.78 (q, OCH ₂); 7.49 (d, 2ArH); 7.89 (d, 2ArH)	
4b ^b 93 c 1665 497 (1.64) 1.33 (s, 2tBu); 2.72 (s, SCH ₃); 305 (3.85) 7.58–7.87 (m, 3ArH) 274 (3.85) 252 (3.79)	
4c ^b 86 c 1661 495 (1.70) 1.28 (s, tBu); 2.73 (s, SCH ₂); 7.28–7.87 (m, 4A 313 (3.94) 272 (4.11) 252 (4.07) 252 (4.07)	rH)
4e 73 126/0.2 1667 497 (1.47) 1.34 (t, CH ₃); 3.32 (q, SCH ₂); 7.20–7.83 (m, 5/ 316 (3.77) 265 (3.84)	ArH)
4f ^b 53 ° 1670 499 (1.62) 1.33 (s, 2tBu); 1.44 (t, CH ₃); 3.42 (q, SCH ₂); 1210 308 (3.86) 7.56–7.68 (m, 3ArH) 271 (4.02) 271 (4.02)	
4g 72 126/0.2 1665 503 (1.63) 1.43 (d, 2CH ₃); 4.18 (sept, SCHMe ₂); 7.30–7.9 317 (3.90) 271 (3.86)	2 (m, 5ArH)
4h 38 ° 1670 1.33 (s, 2tBu); 1.52 (d, 2CH ₃); 4.22 (sept, SCH 1210 7.56–7.65 (m, 3ArH)	Me ₂);
4i ^b 4 ^c 1664 498 (1.86) 1.68 (s, tBu); 7.31–7.91 (m, 5ArH) 315 (3.81) 268 (3.88)	
4j ^b 78 28 1663 500 (1.75) 4.62 (s, SCH ₂); 7.18 (s, 5ArH); 7.30–7.89 (m, 5 316 (3.96) 270 (3.90)	ArH)
5 90 81/9 1734 1.28 (s, tBu); 3.85 (s, OCH ₃) ^d	

^a Elemental analyses in agreement (±0.5%) with theoretical values if not stated otherwise.

^b Elemental analyses deviating (1–2%) from theoretical values due to easy decomposition by hydrolysis, oxidation and elimination of isobutene.

^c Red oil, purified by column chromotagraphy on SiO₂.

^d¹³C NMR (CDCl₃): δ = 25.8[C/CH₃]; 42.7[C(CH₃)₃; 52.1(OCH₃); 164.6(COOCH₃); 202.0(CO-tBu).

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