Formation of acyldisulfide ions from the reaction of sulfur with thiocarboxylate ions, and reactivity towards acyl chlorides in *N*,*N*-dimethylacetamide

Julie Robert, Meriem Anouti and Jacky Paris *

Laboratoire de Physicochimie des Interfaces et des Milieux Réactionnels,
UFR Sciences et Techniques, Parc de Grandmont, 37200 Tours, France

The reactivity of sulfur towards thiocarboxylate ions $RC(O)S^-$ a (R = Ph 1, Me 2, Bu^t 3) has been studied by spectroelectrochemistry in *N*,*N*-dimethylacetamide. For 2a–3a, two parallel and partial reactions, for which equilibrium constants have been determined, led to: (*i*) $[RC(O)]_2S_2^-$ b species and $S_3^{\bullet -}/S_8^{2-}$ polysulfide ions and (*ii*) $RC(O)S_2$ ions c; only traces of 1c were detected by voltammetry. As previously observed with thiolate ions, our results are consistent with an initial monoelectronic transfer between $RC(O)S^-$ ions and S_2 molecules in equilibrium with S_8, followed by concurrent couplings of $RC(O)S^\bullet$ and $S_2^{\bullet -}$ radicals. On a preparative scale, when sulfur was added to $RC(O)S^-$ ions 1a,3a the enhanced reactivity of $RC(O)S_2^-$ ions towards acyl chlorides RC(O)Cl (R = C_6H_5 and Bu^t, respectively) only yielded diacyl disulfides 1b,3b.

In dimethylacetamide (DMA), a dipolar aprotic medium, we recently showed that sulfur reacts with thiolate ions RS^- in two simultaneous ways:[1] (*i*) partial oxidation [reaction (1)] leading

$$RS^- + \tfrac{3}{8}S_8 \longrightarrow \tfrac{1}{2}RS_2R + S_3^{\bullet -} \qquad (1)$$

to RS_2R and polysulfide ions; (*ii*) preponderant reaction (2)

$$RS^- + (x-1)/8\ S_8 \longrightarrow RS_x^- \qquad (2)$$

yielding stable RS_x^- ions (R = alkyl, x = 2–5; R = aryl, x = 2–3).

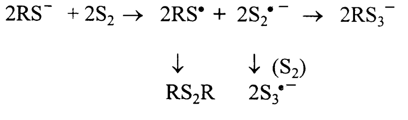
The 'thiophilicity'[2] of RS^- species appeared to be analogous to that of a number of 'S-nucleophiles' Nu[3] (CN^-, SO_3^{2-}, Ar_3P ···). Since the 1950s, the rate-determining step has been believed to involve initial opening [reaction (3)] of the S_8 ring

$$Nu + S_8 \xrightarrow{k} {}^+NuS\text{–}S_6\text{–}S^- \qquad (3)$$

followed by fast and successive displacements of sulfur giving the final product SNu, according to the overall reaction (4).

$$S_8 + 8Nu \longrightarrow 8SNu \qquad (4)$$

A very different mechanism involving reactive S_2 molecules in equilibrium with cyclic S_8[4] was suggested by our group[1] (Scheme 1).



$$\begin{array}{ccccc} 2RS^- + 2S_2 & \rightarrow & 2RS^\bullet & + 2S_2^{\bullet -} & \rightarrow\ 2RS_3^- \\ & & \downarrow & \downarrow (S_2) & \\ & & RS_2R & 2S_3^{\bullet -} & \end{array}$$

Scheme 1

The key redox system $S_2/S_2^{\bullet -}$ should behave like the $O_2/O_2^{\bullet -}$ system in the same type of reactions.[5] After monoelectronic transfer between RS^- and S_2, fast and competing couplings of radicals $RS^\bullet$ and $S_2^{\bullet -}$ entails the simultaneous formation of RS_2R, RS_x^- and polysulfide ions. If alkyl RS_2^-, RS_3^-, RS_4^-, RS_5^- ions can be obtained from the appropriate additions of sulfur, ArS_2^- and ArS_3^- only result from equilibrium reactions (5) and (6) with less basic, reducing and nucleophilic aromatic thiolates than RS^- ions.

$$ArS^- + S_2 \rightleftharpoons ArS_3^- \qquad (5)$$

$$ArS_3^- + ArS^- \rightleftharpoons ArS_2^- \qquad (6)$$

Because of the sulfur–trigonal carbon linkages in both cases we thought that thiocarboxylate ions, like ArS^-, should be able to yield S–S bonds. We report here on the reactivity of sulfur towards the following electrogenerated $RC(O)S^-$ ions in DMA: R = Ph **1**, Me **2**, Bu^t **3**. As with characterization of the $RC(O)SH/RC(O)S^-$ systems, reactions were followed by UV–VIS absorption spectrophotometry coupled with stationary voltammetry. The results were then applied on a preparative scale by addition of acyl chlorides RC(O)Cl to initial $[RC(O)S^- + nS]$ solutions with R = Ph and Bu^t.

Results and discussion

Characteristics of $RC(O)SH/RC(O)S^-$ species in DMA

RC(O)SH species are stronger acids than their homologues RCO_2H, notably in aprotic media; as an example, in dimethyl sulfoxide[6] pK_A (CH_3COSH) = 6.7 and pK_A (CH_3CO_2H) = 12.6. $RC(O)S^-$ ions **1a**–**3a** were generated in low concentrations ($C < 3.6 \times 10^{-3}$ mol dm^{-3}) by electrolysis, under dry nitrogen pressure, of RC(O)SH acids (characteristics in Table 1) at a controlled reduction-wave potential[6] on a gold electrode [reaction (7)].

$$RC(O)SH + e^- \longrightarrow RC(O)S^- + \tfrac{1}{2}H_2 \qquad (7)$$

During oxidation of RCO_2^- ions, decarboxylation of the transient $RCO_2^\bullet$ acyloxy radicals leads to $R^\bullet$ alkyl radicals ('Kolbe reaction'[7]). During electrooxidation of $RC(O)S^-$ [overall reaction (10)], the acyl thioradicals $RC(O)S^\bullet$ dimerize into diacyl disulfides without decomposition.[8]

$$RC(O)S^- - e^- \longrightarrow RC(O)S^\bullet \qquad (8)$$

$$2RC(O)S^\bullet \longrightarrow [RC(O)]_2S_2 \qquad (9)$$

$$2RC(O)S^- - 2e^- \longrightarrow [RC(O)]_2S_2 \qquad (10)$$

Electrolysis of $RC(O)S^-$ ions **1a**–**3a** on their well-defined monoelectronic wave [reaction (10)] entails growth of the $[RC(O)]_2S_2$ wave **1b**–**3b** with an electrical yield >95%. $RC(O)S^-$

Table 1 Electrochemical and spectrophotometric characteristics of thiocarboxylic acids RC(O)SH, diacyldisulfides and thiocarboxylate ions in *N*,*N*-dimethylacetamide. $E_{1/2}$ at a gold-disc electrode *vs.* ref. Ag/AgCl, KCl sat. in DMA/N(Et)$_4$ClO$_4$ 0.1 mol dm^{-3}

	RC(O)SH				RC(O)S$^-$			[RC(O)]$_2$S$_2$		
R	$E_{1/2}$(R)/V	$E_{1/2}$(O)/V	λ_{max}/nm	ε^a_{max}/dm^3 mol^{-1} cm^{-1}	$E_{1/2}$(O)/V	λ_{max}/nm	ε^a_{max}/dm^3 mol^{-1} cm^{-1}	$E_{1/2}$(R)/V	λ_{max}/nm	ε_{max}/dm^3 mol^{-1} cm^{-1}
C_6H_5	−0.86	~+0.87	295	8 800	+0.72	312	5 000	−1.14	268	18 000^b
CH_3	−0.86	~+0.63	257	1 500	+0.31	262	8 000	−1.19	265	3 300^a
Bu^t	−0.92	~+1.1	257	1 400	+0.60	263	7 000	~−1.5	258	3 000^a

^{a} ε/dm^3 mol^{-1} cm^{-1} ± 5%. ^{b} ε ± 10%.

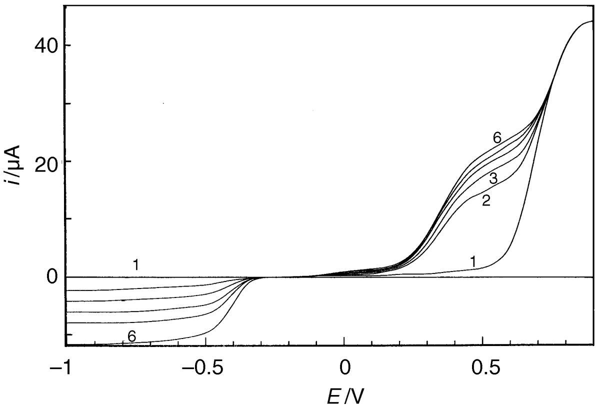


Fig. 1 Evolution of voltammograms during the addition of sulfur to a solution of thiobenzoate ions $C = 3.0 \times 10^{-3}$ mol dm^{-3}. $y = 8[S_8]_0/C = 0$ (1); 0.13 (2); 0.26 (3); 0.43 (4); 0.60 (5); 0.94 (6). Rotating gold-disc electrode $\Omega = 1000$ rev min^{-1}; diameter = 2 mm. *E vs.* reference Ag/AgCl KCl sat. in DMA/N(Et)$_4$ClO$_4$ 0.1 mol dm^{-3}.

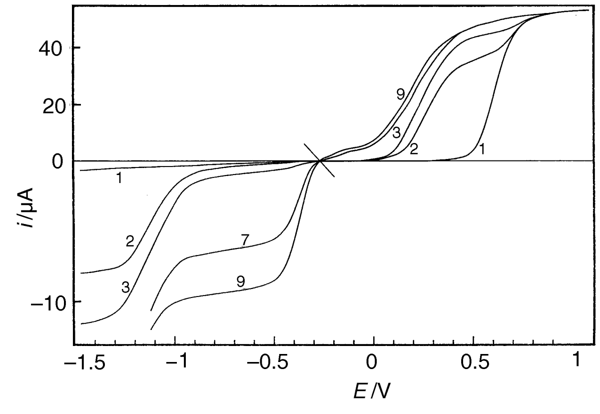


Fig. 2 Evolution of voltammograms during the addition of sulfur to a solution of trimethylthioacetate ions $C = 3.60 \times 10^{-3}$ mol dm^{-3}. $y = 8[S_8]_0/C = 0$ (1); 0.14 (2); 0.28 (3); 0.42 (4); 0.56 (5); 0.70 (6); 0.84 (7); 0.98 (8); 1.12 (9).

ions **1a**–**2a** can be recovered by electroreduction of the diacyl disulfides. Based on their redox behaviour, RC(O)S$^-$/[RC(O)]$_2$S$_2$ mimic RS$^-$/R$_2$S$_2$ systems.[1] The electrochemical and spectrophotometric characteristics of RC(O)S$^-$ and [RC(O)]$_2$S$_2$ obtained in the course of reaction (10) are listed in Table 1.

Reactivity of RC(O)S$^-$ ions with sulfur

The study was carried out in the same way with **1a**–**3a** ions: spectra and voltammograms were recorded at (20.0 ± 0.5) °C during the progressive addition of a concentrated solution of sulfur (8.0×10^{-3} mol dm^{-3}) to $[RC(O)S^-]_0 = C(V = 40$ cm$^3)$ at ratio $y = 8[S_8]_0/C$.

(*a*) With R = C_6H_5, the absorption of RC(O)S$^-$($\lambda_{max} = 312$ nm) remained unchanged and sulfur was completely recovered (Fig. 1, $C = 3.0 \times 10^{-3}$ mol dm^{-3}, $0 < y < 0.94$) from solution, according to the values of its diffusional limiting current $i(R_1)$ [$E_{1/2}$ (R) = −0.40 V *vs.* ref.†] after calibration.[1,4] However, as soon as S_8 was added (curve 2, $y = 0.13$) an oxidation wave appeared at less anodic potentials [$E_{1/2}$(O) ≈ +0.35 V] than that of RC(O)S$^-$ [$E_{1/2}$(O) = +0.72 V] and slightly increased with increasing *y*.

(*b*) With R = Bu^t and $C = 3.6 \times 10^{-3}$ mol dm^{-3}, Figs. 2 and 3 show the i = f(E) and A = f(λ) evolutions as a function of *y* ($0 < y < 1.12$); (i) for $y = 0.14$ (curves 2) the oxidation wave of RC(O)S$^-$ [$E_{1/2}$(O) = +0.60 V] is almost totally displaced ($\Delta E_{1/2} \approx -350$ mV) with total consumption of sulfur [absence of $i(R_1)$]; blue $S_3^{\cdot -}$ ions are detected at low concentrations in the spectra[1,4] ($\lambda^3_{max} = 617$ nm, $\varepsilon^3_{max} = 4390$ dm^3 mol^{-1} cm^{-1}) and another X species absorbs at $\lambda_{max} = 330$ nm; (ii) for $y > 0.14$ (curves 3–8) the first reduction wave R_1 of sulfur appears and the characteristic absorptions of $S_3^{\cdot -}$ ($\lambda^3_{max} = 617$ nm) and

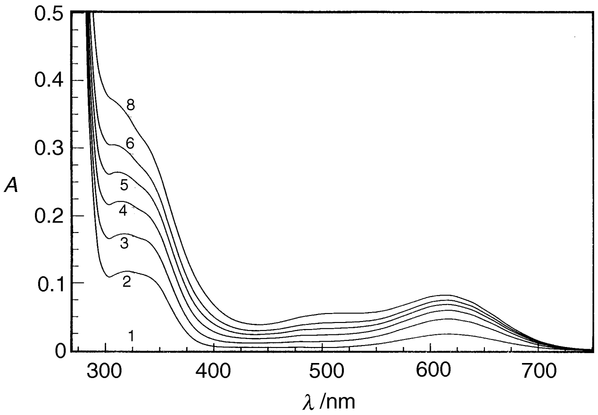


Fig. 3 Evolution of UV–VIS spectra during the reaction of sulfur with trimethylacetate ions. Same conditions as for Fig. 2. Thickness of cell = 0.1 cm.

of S_8^{2-}[1,4] ($\lambda^8_{max1} = 515$ nm, $\varepsilon^8_{max1} = 3800$ dm^3 mol^{-1} cm^{-1}; $\lambda^8_{max2} = 310$ nm, $\varepsilon^8_{max2} = 11\,800$ dm^3 mol^{-1} cm^{-1}) increase because of the equilibrium reaction (11).[1,4] Note that S_8^{2-} ions affect the specific absorption of X at 330 nm.

$$2S_3^{\cdot -} + S_2 \rightleftharpoons S_8^{2-} \qquad (11)$$

(*c*) The addition of sulfur to $CH_3C(O)S^-$ ions entailed the same qualitative behaviour as for **3a**; however, the growth of $A_{617}(S_3^{\cdot -})$ was weaker in proportion, and without the presence of S_8^{2-} and X species gave two absorption bands ($\lambda_{max1} = 336$ nm, $\lambda_{max2} = 467$ nm; $A_1/A_2 \approx 6.0$) as shown in Fig. 4.

These results are in agreement with the competing and partial formations of diacyl disulfides [RC(O)]$_2$S$_2$ **2b**–**3b** and acyl disulfide ions RC(O)S$_2^-$ **2c**–**3c** when sulfur is added to alkylthiocarboxylate ions **2a**–**3a**, as was the case in the course of sulfur–arylthiolate interactions.[1,10]

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† All potentials are expressed in comparison to the reference electrode[9] Ag/AgCl, KCl sat. in DMA/N(Et)$_4$ClO$_4$ 0.1 mol dm^{-3}.

Table 2 Half-wave potentials of reduction and oxidation of $[RC(O)_2]S_2/RC(O)S^-$ systems in the absence or presence of sulfur

R	$E_{1/2}{}^{a}(R)/V$ $[RC(O)]_2S_2$	$E_{1/2}{}^{a}(O)/V$ $RC(O)S^-$	$\lvert\Delta E_{1/2}\rvert/V$	$E_{1/2}(R)/V$ S_8	$E_{1/2}{}^{b}(O)/V$ $RC(O)S_2^-$	$\lvert\Delta E_{1/2}\rvert/V$
C_6H_5	−1.14	+0.72	1.86	−0.40	+0.35	0.75
CH_3	−1.19	+0.31	1.50	−0.40	+0.09	0.49
Bu^t	~−1.5	+0.60	2.1	−0.40	+0.18	0.58

[a] $E_{1/2}$ values of Table 1. [b] $E_{1/2}$ values for $y = 8[S_8]_0/[RC(O)S^-]_0 \approx 1$.

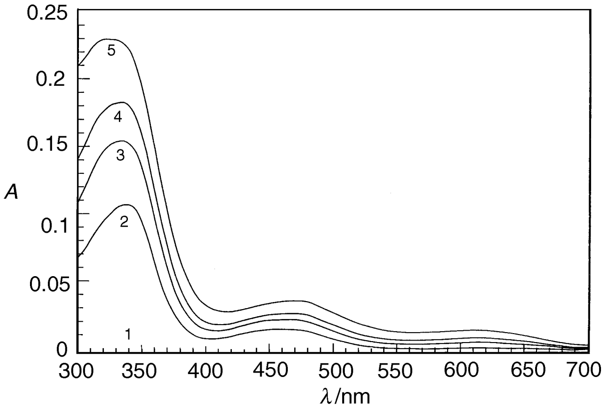

Fig. 4 Evolution of UV–VIS spectra during the addition of sulfur to a solution of thioacetate ions $C = 2.85 \times 10^{-3}$ mol dm^{-3}. $y = 8[S_8]_0/C = 0$ (1); 0.12 (2); 0.24 (3); 0.35 (4); 0.66 (5).

Formation of $RC(O)S_2^-$ species and oxidation of $RC(O)S^-$ ions by sulfur

The shift in the oxidation wave of $RC(O)S^-$ ions towards less oxidizing potentials is typical of the electrocatalytic mechanism in reactions (12) and (13), as observed with alkyl[1] and aromatic[1,10] thiolates.

$$RC(O)S^- + \tfrac{1}{2}S_2 \underset{b}{\overset{f}{\rightleftharpoons}} RC(O)S_2^- \qquad (12)$$

$$RC(O)S_2^- - e^- \longrightarrow \tfrac{1}{2}[RC(O)]_2S_2 + \tfrac{1}{2}S_2 \qquad (13)$$

This phenomenon implies the fast formation [reaction (12)] of $RC(O)S_2^-$ ions **1c**–**3c** and their electrooxidation [reaction (13)] at a greater rate than that of $RC(O)S^-$ into the same species *i.e.* $[RC(O)]_2S_2$, with recovery of sulfur. With R = C_6H_5, sulfur appears as unreactive towards $RC(O)S^-$; the formation of $RC(O)S_2^-$ **1c** is nevertheless evidenced by the presence of its electrocatalytic current ($\Delta E_{1/2} = -0.37$ V). In fact, equilibrium reaction (12) is only displaced by the consumption [reaction (13)] of $C_6H_5C(O)S_2^-$ ions at the electrode surface. Their oxidation wave current is limited by the rate of reaction (12f) as shown by its increase with concentration in sulfur (Fig. 1, curves 2–6).

When the preceding $RC(O)S^-/RC(O)S_2^-$ solutions are progressively oxidized at controlled potential, the limiting current $i(R_1)$ increases up to a greater value than that of the initially added sulfur. The considerable enhancements $i(R_1)_{exp}/i(R_1)_{calc}$‡ which are displayed in Fig. 5 were studied by direct addition of sulfur to diacyl disulfides **1b**–**3b**, obtained by exhaustive oxidation of $RC(O)S^-$ solutions. These observations are consistent with the indirect reduction [reactions (14) and (15)] of $[RC(O)]_2S_2$ species by $S_3{}^{\bullet -}$ or $S_8{}^{2-}$ polysulfide ions.

$$S_8 + 2e^- \longrightarrow S_8{}^{2-} \qquad (14)$$

$$[RC(O)]_2S_2 + S_8{}^{2-} \longrightarrow 2RC(O)S^- + S_8 \qquad (15)$$

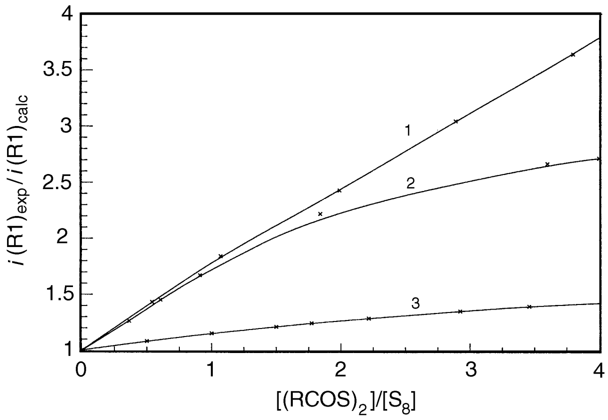

Fig. 5 Relative increase in the first reduction wave of sulfur as a function of $[RC(O)_2S_2]/[S_8]_0$ ratio. R = Ph **1**; Me **2**; Bu^t **3**.

Sulfur, which is regenerated by the fast reaction (15), can be proposed as a mediator in order to facilitate the slow electrode process [reaction (10*b*)] (homogeneous redox catalysis[11]):

$$[RC(O)]_2S_2 + 2e^- \longrightarrow 2RC(O)S^- \qquad (10b)$$

So, $[RC(O)]_2S_2/RC(O)S^-$ redox systems are much less irreversible in the presence of small amounts of sulfur because of the 'simultaneous' catalytic processes, respectively [reactions (14) and (15)], for reduction reaction (10*b*), and reactions (12) and (13) for oxidation reaction (10). This noteworthy effect is illustrated by comparison (Table 2) of $\Delta E_{1/2} = E_{1/2}(O) - E_{1/2}(R)$ in the absence or presence of sulfur. In the last case, the overpotential reduces by more than 1 V.

Simultaneously with the formation of $RC(O)S_2^-$ ions, the partial oxidation of $RC(O)S^-$ ions **2a**–**3a** to $[RC(O)]_2S_2$ **2b**–**3b** occurs with the appearance of $S_3{}^{\bullet -}$ ions ($\lambda^3_{max} = 617$ nm) [reaction (16)].

$$2RC(O)S^- + 3S_2 \rightleftharpoons [RC(O)]_2S_2 + 2S_3{}^{\bullet -} \qquad (16)$$

$S_3{}^{\bullet -}$ ions are also detected on voltammograms by their monoelectronic oxidation and reduction waves[1,4] [$E_{1/2}(O) = -0.20$ V, $E_{1/2}(R)) = -1.10$ V]. However, the reduction current is markedly enhanced (see Fig. 2, curves 2,3) because of the homogeneous catalytic reduction of $[RC(O)]_2S_2$ in the diffusion layer by $S_3{}^{2-}$ ions which are better reducing agents than $S_3{}^{\bullet -}$,[4] reactions (17) and (18).

$$2S_3{}^{\bullet -} + 2e^- \longrightarrow 2S_3{}^{2-} \qquad (17)$$

$$[RC(O)]_2S_2 + 2S_3{}^{2-} \longrightarrow 2RC(O)S^- + 2S_3{}^{\bullet -} \qquad (18)$$

Whatever the oxidation mode of $RC(O)S^-/RC(O)S_2^-$ solutions, electrochemical [reactions (10) and (13)], or chemical by sulfur [reaction (16)], only diacyl disulfides are obtained. Consequently, if the electrochemical reduction reaction (19) of $[RC(O)]_2S_4$ can be conceived, a backward oxidation is impossible.

$$[RC(O)]_2S_4 + 2e^- \longrightarrow 2RC(O)S_2^- \qquad (19)$$

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‡ $i(R_1)_{calc}$ values for sulfur in the absence of diacyl disulfides were obtained by use of the experimental coefficient $i(R_1)/[S_8]_0 = (34.0 \pm 0.5)$ µA mmol^{-1} dm^3, depending on our working gold-disc electrode.

Tetrasulfides were only obtained during reactions between $RC(O)S^-$ and S_2Cl_2.[12]

Because of concurrent formations of $RC(O)S_2^-$ ions [reaction (12)] and $[RC(O)]_2S_2$ species [reaction (16)] in the course of the addition of sulfur to $RC(O)S^-$ ions **2a**–**3a** the following equilibria, together with their corresponding constants, have to be taken into account.

$$S_8 \rightleftharpoons 4S_2 \qquad (20)$$

$$2RC(O)S^- + S_2 \rightleftharpoons 2RC(O)S_2^- \qquad (12)$$

$$2RC(O)S^- + 3S_2 \rightleftharpoons [RC(O)]_2S_2 + 2S_3^{\bullet -} \qquad (16)$$

$$2S_3^{\bullet -} + S_2 \rightleftharpoons S_8^{2-} \qquad (11)$$

$$K_1 = [S_2]^4[S_8]^{-1} = 1.0 \times 10^{-7}\ \text{mol}^3\ \text{dm}^{-9} \qquad (21)$$

$$K_2 = [RC(O)S_2^-]^2[RC(O)S^-]^{-2}[S_2]^{-1} \qquad (22)$$

$$K_3 = [(RCOS)_2][S_3^{\bullet -}]^2[RC(O)S^-]^{-2}[S_2]^{-3} \qquad (23)$$

$$K_4 = [S_8^{2-}][S_3^{\bullet -}]^{-2}[S_2]^{-1} = 0.59 \times 10^6\ \text{dm}^6\ \text{mol}^{-2} \qquad (24)$$

K_1 and K_4 were determined previously in DMA at 297 K. For known initial concentrations $C = [RC(O)S^-]_0$ at definite values of $y = 8[S_8]_0/C$, all concentrations of species in equilibrium can be obtained from constants K_1, K_4 and conservation eqns. (25)–(27).

$$C = [RC(O)S^-] + [RC(O)S_2^-] + 2[(RCOS)_2] \qquad (25)$$

$$8[S_8]_0 = 8[S_8] + 2[S_2] + [RC(O)S_2^-] + 3[S_3^{\bullet -}] + 8[S_8^{2-}] \qquad (26)$$

$$2[(RCOS)_2] = [S_3^{\bullet -}] + 2[S_8^{2-}] \qquad (27)$$

$[S_3^{\bullet -}]$ and $[S_8^{2-}]$ were evaluated from A_{617} and A_{515} measurements on spectra. For y values <0.14 (experimental conditions of Figs. 2–4), sulfur is totally consumed by reactions (12) and (16), and $[RC(O)S_2^-]$ is easily deduced from eqn. (26); ε_{max} of $RC(O)S_2^-$ ions can thus be calculated firstly after substraction of $S_3^{\bullet -}$ (**2a**, **3a**) and S_8^{2-} (**3a**) specific absorbances at A_{max} (values on Fig. 1, ref. 1).

$$\varepsilon_{336}(CH_3COS_2^-) = (4800 \pm 300)\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$$

$$\varepsilon_{467}(CH_3COS_2^-) = (800 \pm 100)\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$$

$$\varepsilon_{330}(Bu^tCOS_2^-) = (4400 \pm 300)\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$$

For each value of $y > 0.14$, S_8 and S_2 concentrations could not be estimated by $i(R_1)$ measurements because of the catalytic currents which were described previously (Fig. 5). $[S_3^{\bullet -}]$, $[S_8^{2-}]$ and $[RCOS_2^-]$ were, respectively, deduced from A_{617}, A_{515} and corrected A_{max} values. These concentrations led to $[S_8]$ and $[S_2]$ with application of eqns. (26) and (21), thus giving access to K_2 and K_3 at 293 K.

$$K_2(CH_3) = (48 \pm 4)\ \text{dm}^3\ \text{mol}^{-1}; \qquad K_3(CH_3) = (12 \pm 2)\ \text{dm}^6\ \text{mol}^{-2}$$

$$K_2(Bu^t) = (81 \pm 8)\ \text{dm}^3\ \text{mol}^{-1}; \qquad K_3(Bu^t) = (1.7 \pm 0.3) \times 10^4\ \text{dm}^6\ \text{mol}^{-2}$$

The compositions of solutions at equilibrium reported in Table 3, with initial **2a**,**3a** concentrations (C) from Figs. 2–4, and $y = 1$ were calculated by the use of K_2 and K_3.

ArS_2^- species are better nucleophiles than the corresponding thiolates:[13] when $Ar = 4\text{-}NO_2C_6H_4$, the reaction rates (S_N2 mechanism) of ArS_2^- with alkyl halides increased by a factor of 10 in comparison with those of ArS^-, regardless of the nature of RX (C_2H_5I, C_3H_7I, C_3H_7Br). The reactivity of $RC(O)S^-$ ions, alone or in the presence of sulfur, has been tested with regard to some acyl chlorides.

Table 3 Composition at equilibrium (mol R%) after addition of sulfur ($y = 8[S_8]_0/C = 1$) to C solutions of thiocarboxylate ions **2a** ($R = CH_3$), **3a** ($R = Bu^t$)

Species	$C/10^{-3}$ mol dm^{-3}	**a** (%)	**b** (%)	**c** (%)
2a	2.85	81	2	17
3a	3.60	68	15	17

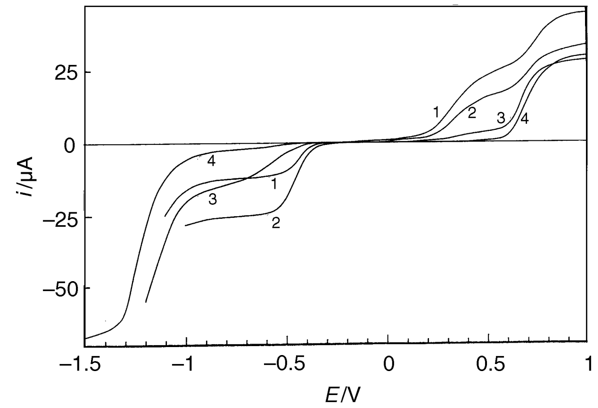

Fig. 6 Evolution of voltammograms during the addition of benzoyl chloride to a solution $[C_6H_5C(O)S^-]_0 = 2.80 \times 10^{-3}$ mol dm^{-3} + $8[S_8]_0 = 2.64 \times 10^{-3}$ mol dm^{-3}. $[RC(O)Cl]/C$ = 0 (1); 0.27 (2); 0.54 (3); 0.98 (4).

Reactivity of $RC(O)S^-/RC(O)S_2^-$ ions towards acyl chlorides

Alkyl halides are known for undergoing rapid nucleophilic substitutions with $RC(O)S^-$ ions to produce thioesters, whose methods of preparation have been reviewed.[14] When benzyl bromide is added to $CH_3C(O)S^-$ ions in DMA, their anodic wave [$E_{1/2}(O) = +0.31$ V] decreases at the expense of the oxidation current of Br^- ions[15] [$3Br^- \longrightarrow Br_3^- + 2e^-$, $E_{1/2}(O) \approx +0.70$ V] according to the stoichiometry in reaction (28).

$$C_6H_5CH_2Br + CH_3C(O)S^- \longrightarrow CH_3C(O)SCH_2C_6H_5 + Br^- \qquad (28)$$

In the same way, acyl chlorides RC(O)Cl readily react [reaction (29)] with $RC(O)S^-$ ions, with the appearance of Cl^- ions

$$RC(O)Cl + RC(O)S^- \longrightarrow [RC(O)]_2S + Cl^- \qquad (29)$$

[$E_{1/2}(O) \approx +0.65$ V] at the expense of $RC(O)S^-$, and the growth of a reduction wave only for $[C_6H_5C(O)]_2S$ [$E_{1/2}(R) = -1.29$ V].

On a preparative scale (see Experimental), the addition of $C_6H_5CH_2Br$ or $C_6H_5C(O)Cl$ at 40 °C to electrogenerated $RC(O)S^-$ ions [$CH_3C(O)S^-$ and $C_6H_5C(O)S^-$, respectively] afforded the expected products: $CH_3C(O)SCH_2C_6H_5$ (yield 78%) and $[C_6H_5C(O)]_2S$ (67%) were identified by GC–MS, ^1H and ^{13}C NMR spectroscopies.

The progress of the reaction between benzoyl chloride and a solution $[C_6H_5C(O)S^-]_0 = 2.80 \times 10^{-3}$ mol dm^{-3} + $8[S_8]_0 = 2.64 \times 10^{-3}$ mol dm^{-3} ($y = 0.94$) is shown by the voltammetric recordings in Fig. 6: during consumption of $RC(O)S^-$ ions [decrease of their anodic current at the expense of Cl^-, $E_{1/2}(O) \approx +0.65$ V], the formation of $[C_6H_5C(O)]_2S_x$ entails at first (curve 2) a catalytic growth in the reduction wave of sulfur [$E_{1/2}(R) \approx -0.40$ V], then a considerable drop in intensity (curves 3,4) as if S_8 were completely consumed. Dibenzoyl disulfide [$E_{1/2}(R) = -1.14$ V] can be proposed as the major product of the overall reaction (30), even if only traces of $RC(O)S_2^-$ ions

$$\mathrm{RC(O)Cl + RC(O)S^- + \tfrac{1}{2}S_2 \longrightarrow [RC(O)]_2S_2 + Cl^-} \qquad (30)$$

were previously evidenced during the reaction of sulfur with $\mathrm{RC(O)S^-}$ species ($\mathrm{R = C_6H_5}$).

This assumption was confirmed by two synthesis [$\mathrm{R = C_6H_5}$, $\mathrm{(CH_3)_3C}$] based on reaction (30) [electrogenerated $\mathrm{RC(O)S^-}$ ions **1a**,**3a**; addition of sulfur in excess ($y \approx 2$); addition of RC(O)Cl]: $\mathrm{[(CH_3)_3CC(O)]_2S_2}$ was the only product isolated (yield 72%) whereas $\mathrm{[C_6H_5C(O)]_2S_2}$ greatly predominated over $\mathrm{[C_6H_5C(O)]_2S}$ (~93/7). And yet mixtures $\mathrm{[RC(O)]_2S/[RC(O)]_2S_2}$ could be expected from reactions between acyl chlorides and thiocarboxylate ions in the presence of sulfur according to moderately displaced equilibrium reaction (12) in favour of $\mathrm{RC(O)S_2^-}$ ions. The electron delocalization induced by the carbonyl group in $\mathrm{RC(O)S^-}$ is very much lowered in $\mathrm{RC(O)S_2^-}$ anions, probably because the S–S bond does not transmit the conjugation.[16] The great increase in reactivity of $\mathrm{RC(O)S_2^-}$ ions in comparison with that of $\mathrm{RC(O)S^-}$, as was the case for $\mathrm{ArS_2^-/ArS^-}$ species, has been rationalized in terms of the 'α-effect';[17] this effect is generally observed when unshared electron pairs lie on an atom adjacent to a nucleophilic centre ($\mathrm{ClO^-, RO_2^-} \cdots$).

Experimental

Materials and equipment

All thiocarboxylic acids RC(O)SH (R = Me, $\mathrm{Bu^t}$, Ph) and acyl chlorides, obtained from Aldrich (as well as DMA), were distilled under dry nitrogen just before use. Solvent purification and storage after addition of $\mathrm{N(Et)_4ClO_4}$ (Fluka) 0.1 mol $\mathrm{dm^{-3}}$ as supporting electrolyte have been reported elsewhere.[9] Spectroelectrochemical equipments, electrodes, the thermostatted flow-through cell and the two-compartment preparative cell were the same as previously described.[4,15] Analysis and identification of the synthesized products were performed by GC–MS spectrometry (Hewlett-Packard 5989A, EI 70 eV), ^{1}H (200.132 MHz) and ^{13}C (50.323 MHz) NMR spectroscopy (Bruker AC 200 spectrometer, $\mathrm{CDCl_3}$ as solvent, J values in Hz).

Preparative electrolysis

The reactions of $\mathrm{RC(O)S^-}$ ions, alone or in the presence of sulfur, with acyl chlorides (or benzyl bromide) were carried out in the same way on a preparative scale: 0.8–1 g of thiocarboxylic acid was dissolved in 120 $\mathrm{cm^3}$ of the catholyte $\mathrm{N(Et)_4ClO_4}$ 0.5 mol $\mathrm{dm^{-3}}$ in DMA and electrolysed at controlled potential ($-1.5\ \mathrm{V} < E < -1.2\ \mathrm{V}$) on a large gold grid electrode, within 2 h. When used, solid sulfur in powder form was then poured in the cathodic compartment. Acyl chloride or benzyl bromide dissolved in 20 $\mathrm{cm^3}$ of DMA was added in deficit (mol. 90%) with respect to initial RC(O)SH. After heating at 40 °C during 10 min, the reaction medium was diluted with 4 vol. of 3% aqueous $\mathrm{NaHCO_3}$ before extraction with diethyl ether. The organic phase was thoroughly washed with water in order to eliminate traces of DMA and dried ($\mathrm{MgSO_4}$).

The oily products $\mathrm{CH_3C(O)SCH_2C_6H_5}$ and $\mathrm{[(CH_3)_3CC(O)]_2S_2}$ were purified by column chromatography on silica gel with light petroleum–diethyl ether (80 : 20) as eluent. The crude compounds $\mathrm{[C_6H_5C(O)]_2S}$ and $\mathrm{[C_6H_5C(O)]_2S_2}$ were recrystallized respectively from dichloromethane–light petroleum and 1,2-dichloroethane.

Reaction of thioacetate ions 2a and benzyl bromide. Thioacetic acid: 0.835 g (10.97 mmol); benzyl bromide: 1.69 g (9.87 mmol). Product: *S*-benzyl thioethanoate (1.28 g, 78%); δ_H 2.40 (3 H, s, Me), 4.18 (2 H, s, $\mathrm{CH_2}$) and 7.27–7.35 (5 H, m); δ_C 30.1, 33.4, 127.3, 128.7 (2 C), 128.9 (2 C), 138.8 and 194.7; *m/z* 166 ($\mathrm{M^+}$, 16%), 123 (16), 122 (15), 91 (95), 65 (16) and 43 (100).

Reaction of thiobenzoate ions 1a and benzoyl chloride. Thiobenzoic acid: 0.995 g (7.20 mmol); benzoyl chloride: 0.91 g (6.48 mmol). Product: dibenzoyl sulfide (1.05 g, 67%), mp 45–47 °C (lit.,[18] 47–48 °C); δ_H 7.51–7.73 (6 H, m) and 8.06 (4 H, d, J 7.4); δ_C 127.4 (4 C), 128.7 (4 C), 133.8 (2 C), 135 (2 C) and 186 (2 C); *m/z* 242 ($\mathrm{M^+}$, <2%), 105 (100), 77 (55) and 51 (25).

Reaction of 1a and benzoyl chloride in the presence of sulfur. Thiobenzoic acid: 0.827 g (6.0 mmol); $\mathrm{S_8}$ 0.391 g (12.2 mmol S); benzoyl chloride: 0.757 g (5.38 mmol). Products: 1.18 g (~80%); from δ_H(4 H, d), dibenzoyl disulfide (~93%) and dibenzoyl sulfide (~7%). Dibenzoyl disulfide: mp 135–136 °C (lit.,[19] 136–136.5 °C): δ_H 7.53–7.75 (6 H, m) and 8.13 (4 H, d, J 7.4); δ_C 128.1 (4 C), 129 (4 C), 133.8, 134 (2 C) and 186 (2 C); direct introduction mode *m/z* 274 ($\mathrm{M^+}$, 4%), 105 (50), 77 (100) and 51 (25).

Reaction of 3a and trimethylacetyl chloride in the presence of sulfur. Trimethyl thioacetic acid: 0.944 g (7.98 mmol); $\mathrm{S_8}$: 0.506 g (15.8 mmol S); trimethylacetyl chloride: 0.865 g (7.17 mmol). Product: di(trimethylacetyl) disulfide (1.21 g, 72%), δ_H 1.37 (18 H, s); δ_C 27 (6 C), 46.8 (2 C) and 199 (2 C); *m/z* 234 ($\mathrm{M^+}$, <2%), 85 (53), 57 (100) and 41 (11).

Conclusions

Alkylthiocarboxylate ions behave towards sulfur like arylthiolates bearing electron-withdrawing groups. In both cases, the competing formation of disulfide ions and oxidation into disulfide moleclules were low; for example, from known equilibrium constants K_2 and K_3 in DMA,[10] the addition of sulfur ($y = 1$) to $\mathrm{[4\text{-}NO_2C_6H_4S^-]_0} = 3.0 \times 10^{-3}$ mol $\mathrm{dm^{-3}}$ led us to calculate (Ar%) 80% $\mathrm{ArS^-}$, 15% $\mathrm{ArS_2^-}$, 5% $\mathrm{Ar_2S_2}$ at equilibrium. As shown with thiolate ions, the reaction between thiocarboxylate ions and sulfur is consistent with an initial monoelectronic transfer reaction (31).

$$\mathrm{RC(O)S^- + S_2 \rightleftharpoons RC(O)S^\bullet + S_2^{\bullet -}} \qquad (31)$$

Concurrent couplings of intermediate radicals again yield, on the one hand, diacyl disulfides and polysulfide ions, and on the other hand, acyldisulfide ions. All species are in equilibrium, thiocarboxylates being of weaker reducing power than thiolates.

In the presence of sulfur the enhanced reactivity of thiocarboxylate ions towards acyl chlorides leads to the noteworthy formation of diacyl disulfides.

The present results will be invoked to explain the nucleophilic substitution of $\mathrm{S_3^{\bullet -}}$ ions on acyl chlorides.

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