

Nucleophilic substitution of acyl chlorides by electrogenerated polysulfide ions in *N,N*-dimethylacetamide



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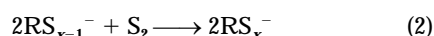
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The reactions between acyl chlorides RC(O)Cl (**a**) [$\text{R} = \text{Me}$ (**1**), Pr^i (**2**), Bu^t (**3**), Ph (**4**)] and electrogenerated $\text{S}_3^{\cdot-}$ ($\rightleftharpoons \text{S}_6^{2-}$) ions have been investigated in *N,N*-dimethylacetamide by spectroelectrochemistry. With $\text{R} = \text{alkyl}$, thiocarboxylate ions and sulfur resulting from the fast initial substitutions cause partial formation of both acyl disulfide ions and diacyl disulfides (**b**) at a γ ratio $[\text{RC(O)Cl}]/[\text{S}_3^{\cdot-}]$ of 0.5; the second step stoichiometrically ($\gamma = 1$) affords diacyl disulfides **1b–4b** as the presumed products. The formation of these species only is confirmed on a preparative scale from two sets of experiments: (i) direction addition of acyl chlorides (**1a–4a**) to chemically generated $\text{S}_3^{\cdot-}$ solutions; (ii) electrolysis of sulfur in the presence of acyl chlorides **2a–4a**.

The nucleophilic reactivity of polysulfide ions $\text{S}_3^{\cdot-}$ ($\rightleftharpoons \text{S}_6^{2-}$) and S_8^{2-} in *N,N*-dimethylacetamide (DMA), a dipolar aprotic solvent, has been the subject of several reports by our group.¹ With alkyl halides RX , the $\text{S}_\text{N}2$ reactions led to dialkyl tri- and tetra-sulfides,^{1a} with probable transient RS_x^- ions ($x = 3, 4$). *o*- and *p*-nitrophenyl disulfide ions $\text{NO}_2\text{C}_6\text{H}_4\text{S}_2^-$ were obtained from $\text{S}_\text{N}\text{Ar}$ processes on nitroaromatic halides^{1b} or dinitrobenzenes.^{1d} However, we showed that sulfur reacts with thiolate ions RS^- in two parallel ways:² (i) oxidation (1) into RS_2R , (ii)



preponderant and successive formation (2) of RS_{x-1}^- ions



($\text{R} = \text{alkyl}$,² $x = 2-5$; $\text{R} = \text{aryl}$,^{2,3} $x = 1-3$; $\text{R} = 2-$ or $4-\text{NO}_2\text{C}_6\text{H}_4$,³ $x = 1-2$ in equilibrium). These results were consistent with, at first, a mono-electronic transfer between RS^- ions and the reactive S_2 molecule² in equilibrium with cyclic S_8 .⁴ The redox system $\text{S}_2/\text{S}_2^{\cdot-}$ behaves like the $\text{O}_2/\text{O}_2^{\cdot-}$ one in the same type of nucleophilic reactions: $\text{RX} + \text{O}_2^{\cdot-}$ ($\text{S}_\text{N}2^5$), $\text{ArX} + \text{O}_2^{\cdot-}$ ($\text{S}_\text{N}\text{Ar}^6$) or redox processes such as $\text{RS}^- + \text{O}_2$,⁷ with the difference that $\text{S}_2^{\cdot-}$ can dimerize into S_4^{2-} ions.^{2,4}

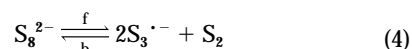
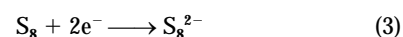
In a recent paper,⁸ we reported that electrogenerated thiocarboxylate ions were also able to give S–S bonds in the presence of sulfur, with the same behaviour as arenethiolates bearing an electron-withdrawing group (e.g. $4-\text{NO}_2\text{C}_6\text{H}_4\text{S}^-$); when RC(O)Cl ($\text{R} = \text{Ph}$, Bu^t) were added to $[\text{RC(O)S}^- + \text{S}_2]$ solutions, only diacyl disulfides were obtained on a preparative scale. $\text{O}_2^{\cdot-}$ ions react with acyl chlorides⁹ and anhydrides¹⁰ in aprotic solvents, yielding diacyl peroxides. Here we examine the reactivity of electrogenerated $\text{S}_3^{\cdot-}$ ions towards a series of RC(O)Cl species (**a**) [$\text{R} = \text{Me}$ (**1**), Pr^i (**2**), Bu^t (**3**), Ph (**4**)] by UV–VIS absorption spectrophotometry coupled with stationary voltammetry. The results were then confirmed by synthesis and electro-synthesis.

Results

Sulfur–polysulfide ions and thiocarboxylate–acyl disulfide ions characteristics in DMA

In aprotic media such as DMA, sulfur reduces into two bi-electronic steps with respect to S_8 ⁴ (waves R_1 and R_2) on a rotating gold-disc electrode. The stable product of the electrolysis at controlled potential on R_1 is the blue anion radical $\text{S}_3^{\cdot-}$

($\lambda_{\text{max}} = 617 \text{ nm}$) through the disproportionation (4) of the red



$$K_1 (297 \text{ K}) = [\text{S}_3^{\cdot-}]^2[\text{S}_2][\text{S}_8^{2-}]^{-1} = 1.7 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6} \quad (5)$$



$$K_2 = [\text{S}_2]^4[\text{S}_8]^{-1} = 10^{-7} \text{ mol}^3 \text{ dm}^{-9} \quad (7)$$

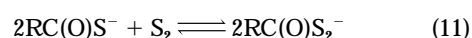
S_8^{2-} ions ($\lambda_{\text{max}} = 515 \text{ nm}$). The elimination of sulfur at $\frac{8}{3}\text{F mol}^{-1}$ S_8 leads to $\text{S}_3^{\cdot-}$ species i.e. $\text{S}_3^{\cdot-}$ ions in equilibrium (8) with



$$K_3 (297 \text{ K}) = [\text{S}_3^{\cdot-}]^2[\text{S}_6^{2-}]^{-1} = 0.043 \text{ mol dm}^{-3} \quad (9)$$

their dimer S_6^{2-} ($\lambda_{\text{max}} = 465 \text{ nm}$). In dilute solutions, $[\text{S}_6^{2-}]$ remains low in comparison with $[\text{S}_3^{\cdot-}]$; as an example, for $[\text{S}_3^{\cdot-}]_{\text{T}}^0 = [\text{S}_3^{\cdot-}]_0 + 2[\text{S}_6^{2-}]_0 = 5.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{S}_3^{\cdot-}]_0 = 4.16 \times 10^{-3} \text{ mol dm}^{-3}$ and $[\text{S}_6^{2-}]_0 = 0.42 \times 10^{-3} \text{ mol dm}^{-3}$. S_8^{2-} and $\text{S}_3^{\cdot-}$ ions oxidize (O_1) and reduce (R_2) at the same potentials.

$\text{RC(O)S}^-/\text{RC(O)S}_2^-$ ions will be implicated in the course of the reactions between RC(O)Cl molecules and $\text{S}_3^{\cdot-}$ ions. Some of these ions ($\text{R} = \text{Me}$, Bu^t , Ph) have been studied earlier after electroreduction of thiocarboxylic acids and addition of sulfur:⁸ with $\text{R} = \text{alkyl}$, the equilibria (10) and (11), analogous to



$$K_4 = [(\text{RCOS})_2][\text{S}_3^{\cdot-}]^2[\text{RC(O)S}^-]^{-2}[\text{S}_2]^{-3} \quad (12)$$

$$K_5 = [\text{RC(O)S}_2^-]^2[\text{RC(O)S}^-]^{-2}[\text{S}_2]^{-1} \quad (13)$$

$$K_4 (\text{Me}) = (12 \pm 2) \text{ dm}^6 \text{ mol}^{-2}; K_5 (\text{Me}) = (48 \pm 4) \text{ dm}^3 \text{ mol}^{-1}$$

$$K_4 (\text{Bu}^t) = 1.7 \pm 0.3 \times 10^4 \text{ dm}^6 \text{ mol}^{-2}; K_5 (\text{Bu}^t) = (81 \pm 8) \text{ dm}^3 \text{ mol}^{-1}$$

Table 1 Spectrophotometric and electrochemical characteristics of sulfur/polysulfide ions⁴ and thiocarboxylate-acyl disulfide ions⁸ in *N,N*-dimethylacetamide. E_i^0 at a rotating gold-disc electrode vs. ref. Ag/AgCl(s), KCl_{sat.} in DMA/N(Et)₄ClO₄ (0.1 mol dm⁻³)

Parameter	S ₈	S ₈ ²⁻	S ₃ ^{·-}	RC(O)S ⁻ /R			RC(O)S ₂ ⁻ /R		
				1	3	4	1	3	4
λ_{\max}/nm	262 (8.0)	515 (3.8)	617 (4.4)	262 (8.0)	263 (7.0)	312 (5.0)	336 (4.8)	330 (4.4)	—
$(\epsilon_{\max})^a$		360 (9.0)					467 (0.8)		O (0.35) ^c
Wave (E_i^0/V)	R ₁ (-0.40)	R ₂ (-1.10)	R ₂	O (0.31)	O (0.60)	O (0.72)	O (0.09)	O (0.18)	
	R ₂ (-1.10)	O ₁ (-0.20)	O ₁						
i/c^b	R ₁ (34)	O ₁ (26.5)	R ₂ (16)	14	14	16			
	R ₂ (35)		O ₁ (16)						

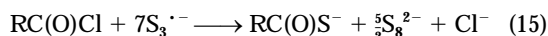
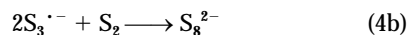
^a $\epsilon/10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. ^b i = limiting current for each species alone in solution; i/c values ($\mu\text{A mol}^{-1} \text{ dm}^3$) at the same rotating gold disc electrode (diameter = 2 mm; $\Omega = 1000 \text{ rev min}^{-1}$). ^c In the presence of sulfur, the formation of C₆H₅C(O)S₂⁻ ions is observed in the lone diffusion layer.

(1) and (2) were evidenced. Spectrophotometric (λ_{\max} , ϵ_{\max}) and electrochemical [$E_i^0(O)$, $E_i^0(R)$] characteristics of sulfur/polysulfide ions and those of RC(O)S⁻/RC(O)S₂⁻ ions are summarized in Table 1. [S₃^{·-}], [S₆²⁻], [S₈²⁻] can be accurately evaluated from A_{617} , A_{515} measurements and the values of K_1 , K_2 , K_3 ; [S₈] could be obtained by the limiting intensity of its R₁ wave.

Reactivity of S^{·-} ions towards acyl chlorides

Acyl chlorides are very sensitive to hydrolysis into RCO₂H and HCl acids. The carboxylic acids are practically unreactive with S^{·-} and S₈²⁻ polysulfides in dimethylacetamide [$pK_A(\text{CH}_3\text{CO}_2\text{H}) = 12.6$;¹¹ $pK_A(\text{C}_6\text{H}_5\text{CO}_2\text{H}) = 11.0$ ¹¹] whereas hydrochloric acid results in the oxidation of S₃^{·-} into S₈²⁻ and the protonation of these weak basic species¹² [$9 < pK_A(\text{HS}_8^-) < 11$, $7 < pK_A(\text{H}_2\text{S}_8) < 9$]. All the substrates RC(O)Cl were carefully distilled on molecular sieves under dry nitrogen atmosphere just before use.

The reactions were followed at room temperature by spectroelectrochemistry during the addition of a concentrated solution of acyl chloride (1a–4a) in DMA ($3 \times 10^{-2} \text{ mol dm}^{-3} < C < 1.5 \times 10^{-1} \text{ mol dm}^{-3}$) to S^{·-} ions of total concentration [S₃^{·-}]_T^o close to $5.0 \times 10^{-3} \text{ mol dm}^{-3}$. The stoichiometric processes described below indicated that effective RC(O)Cl concentrations were ~92 (R = Me, Prⁱ) to 95% (R = Bu^t, Ph) of theoretical values. In all cases, the reactions were fast under our experimental conditions. Figs. 1(a) and (b) and 2 show the general evolutions of UV–VIS spectra and voltammograms when RC(O)Cl (R = alkyl, 1a–3a) were progressively added to S^{·-} solutions, after the example RC(O)Cl = Bu^tC(O)Cl + [S₃^{·-}]_T^o = $5.17 \times 10^{-3} \text{ mol dm}^{-3}$; as long as the ratio $y = [\text{RC(O)Cl}]_{\text{ad.}}/[\text{S}_3^{\cdot-}]_{\text{T}}^{\text{o}}$ remains below 0.15 (~1/7), A_{617} (S₃^{·-}) decreases while the bands of S₈²⁻ increase ($\lambda_{\max 1} = 515 \text{ nm}$, $\lambda_{\max 2} = 360 \text{ nm}$) with the occurrence of an isosbestic point at 540.5 nm [Fig. 1(a)]. The calculated variations of [S₃^{·-}]_T and [S₈²⁻] satisfy $\Delta[\text{S}_8^{2-}]/\Delta[\text{S}_3^{\cdot-}]_{\text{T}} \approx -5/14$, and agree with the overall eqn. (15) = (14) + $\frac{5}{2}$ (4b). The consump-



tion of sulfur arising from substitution (14) is practically quantitative according to eqn. (4b) because of the excess in S₃^{·-} ions and of the values of K_1 and K_2 . The stoichiometry (15) with $7\text{S}_3^{\cdot-} \longrightarrow \frac{5}{2}\text{S}_8^{2-}$ ($\lambda_{\text{is}} = 540 \text{ nm}$) was already observed in the course of the substitutions of S₃^{·-} ions on *o*- and *p*-nitroaromatics NO₂C₆H₄X (X = halides,^{1b} NO₂^{1d}). For $0.15 < y < 0.5$, the reactions of both S₃^{·-} and S₈²⁻ ions [decreases of A_{617} , A_{515} ; $i(O_1)$, $E_i^0 = -0.20 \text{ V}$] entail the appearance of S₈ [$i(R_1)$, $E_i^0 = -0.40 \text{ V}$], RC(O)S⁻/RC(O)S₂⁻ [$i(O) \approx +0.17 \text{ V}$] and Cl⁻ [$E_i^0(O) \approx +0.65 \text{ V}$] ions. In the presence of sulfur, RC(O)S⁻ and RC(O)S₂⁻ in equilibrium (11) are detected

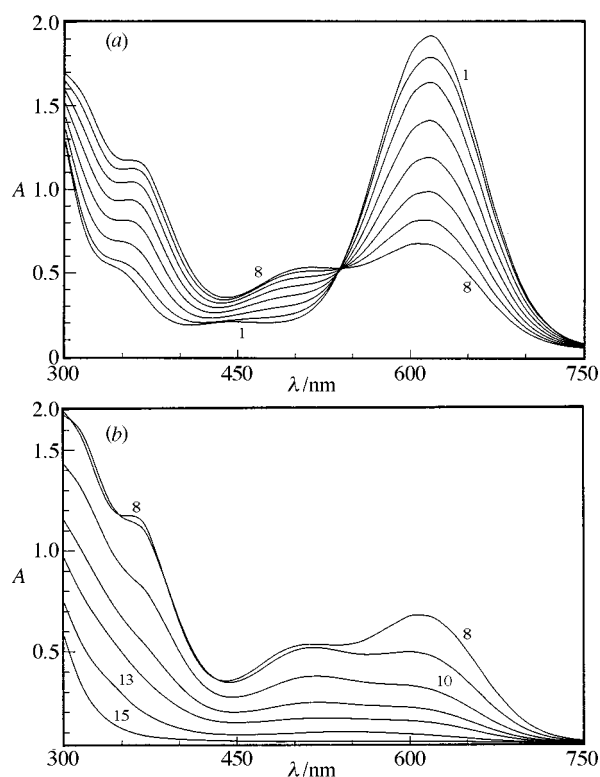
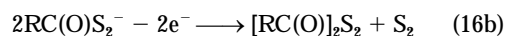
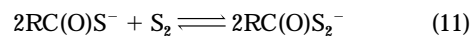
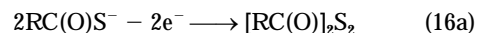


Fig. 1 Evolution of UV–VIS spectra during addition of *tert*-butyl acetyl chloride to a S₃^{·-} solution [S₃^{·-}]_T^o = $5.17 \times 10^{-3} \text{ mol dm}^{-3}$. (a) $y = [\text{RC(O)Cl}]/[\text{S}_3^{\cdot-}]_{\text{T}}^{\text{o}} = 0$ (1); 0.02 (2); 0.04 (3); 0.06 (4); 0.08 (5); 0.11 (6); 0.13 (7); 0.15 (8). (b) $y = 0.15$ (8); 0.20 (9); 0.31 (10); 0.42 (11); 0.53 (12); 0.75 (13); 0.96 (14); 0.99 (15). Thickness of the cell 0.1 cm.

by the same oxidation wave⁸ according to the electrocatalytic process (11) + (16b), as previously observed with thiolate



ions.² For $y = 0.5$ [stoichiometry (14)] the polysulfides S₈²⁻ and S₃^{·-} are not completely eliminated as shown by the persistence of A_{515} , A_{617} and $i(O_1)$ [Figs. 1(b) and 2, curves 12]. The spectra are the same as those of RC(O)S⁻ solutions electrogenerated from RC(O)SH and added to sulfur in a proportion of $8[\text{S}_8]_0/[\text{RC(O)S}^-]_0 = 5$; this was verified between $[\text{S}_3^{\cdot-}]_{\text{T}}^{\text{o}} = 4.97 \times 10^{-3} \text{ mol dm}^{-3}$ + [MeC(O)Cl]₀ = $2.58 \times 10^{-3} \text{ mol dm}^{-3}$ ($y = 0.52$) and $[\text{CH}_3\text{C(O)S}^-]_0 = 2.25 \times 10^{-3} \text{ mol dm}^{-3}$ + $8[\text{S}_8]_0 = 11.0 \times 10^{-3} \text{ mol dm}^{-3}$. The concentrations which were evaluated by the use of K_1 , K_2 , K_4 and K_5 constants (R = Me, Bu^t, conditions of Table 2) led to values of A_{515} and A_{617} in agreement ($\pm 10\%$) with the experimental one. For

Table 2 Calculated composition (mmol dm^{-3}) of solutions of thiocarboxylate ions ($R = \text{Me}, \text{Bu}^t$) added with sulfur; $[\text{RC}(\text{O})\text{S}^-]_0 = 2.60 \times 10^{-3} \text{ mol dm}^{-3} + 8[\text{S}_8]_0 = 13.0 \times 10^{-3} \text{ mol dm}^{-3}$

R	$\text{RC}(\text{O})\text{S}^-$	$\text{RC}(\text{O})\text{S}_2^-$	$(\text{RCO})_2\text{S}_2$	$\text{S}_3^{\cdot-}$	S_8^{2-}	RCOS_2^- (%) ^a	$(\text{RCO})_2\text{S}_2$ (%) ^b
Me	1.80	0.63	0.08	0.12	0.02	24	6
Bu^t	0.83	0.38	0.70	0.54	0.42	14.6	53.8

^a RCOS_2^- (%) = $[\text{RC}(\text{O})\text{S}_2^-]/[\text{RC}(\text{O})\text{S}^-]_0$, ^b $(\text{RCO})_2\text{S}_2$ (%) = $2[(\text{RCO})_2\text{S}_2]/[\text{RC}(\text{O})\text{S}^-]_0$.

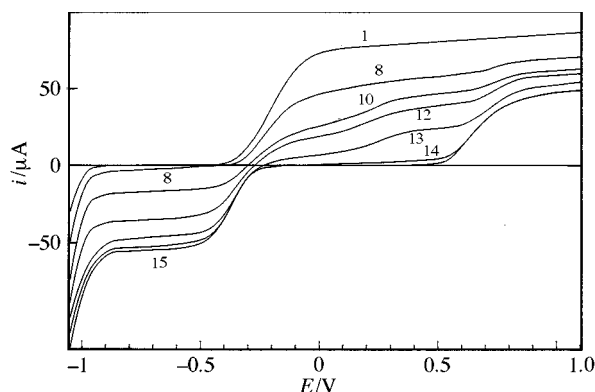
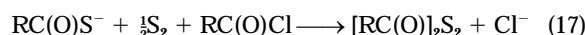


Fig. 2 Evolution of voltammograms during the reaction of *tert*-butylacetyl chloride with $\text{S}_3^{\cdot-}$ ions. Same conditions as for Fig. 1. Rotating gold-disc electrode, $\Omega = 1000 \text{ rev min}^{-1}$, diameter = 2 mm. E vs. reference $\text{Ag}/\text{AgCl}(\text{s})$, KCl sat. in $\text{DMA}-\text{N}(\text{Et})_4\text{ClO}_4$ (0.1 mol dm^{-3}).

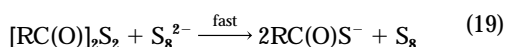
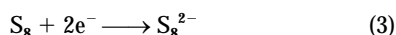
$y > 0.5$, $\text{S}_3^{\cdot-}$, S_8^{2-} and $\text{RC}(\text{O})\text{S}^-/\text{RC}(\text{O})\text{S}_2^-$ concentrations continue to decrease, as shown by the variations of visible absorbances and oxidation currents [Figs. 1(b) and 2, curves 13, 14]. When y reaches the value 1.0, the solutions ($R = \text{alkyl}$) were decoloured and the wave of Cl^- ions ($3\text{Cl}^- \rightarrow \text{Cl}_3^- + 2\text{e}^-$) was the only anodic one, with an intensity close to that calculated after calibration with a solution of $\text{N}(\text{CH}_3)_4\text{Cl}$ [$i(\text{O})/C \approx 8 \mu\text{A mmol}^{-1} \text{ dm}^3$]. $\text{C}_6\text{H}_5\text{C}(\text{O})\text{S}^-$ ions are not oxidized by sulfur into diacyl disulfide and polysulfide ions⁸ [eqn. (10)], so when benzoyl chloride was added to $\text{S}_3^{\cdot-}$ ions, the consumption of $\text{S}_3^{\cdot-}/\text{S}_8^{2-}$ ions went to completion for $y = 0.5$. However, in the presence of sulfur, all the $\text{RC}(\text{O})\text{S}^-$ ions ($R = \text{alkyl}, \text{phenyl}$) react with $\text{RC}(\text{O})\text{Cl}$ yielding $[\text{RC}(\text{O})]_2\text{S}_2$ species (**b**)⁸ [eqn. (17)].



The overall reaction of acyl chlorides with $\text{S}_3^{\cdot-}$ ions can thus be summarized by eqn. (18).



Fig. 3 sums up the evolution of concentrations $[\text{S}_3^{\cdot-}]_T$, $[\text{S}_8^{2-}]$, $[\text{RC}(\text{O})\text{S}_x^-]$ ($x = 1, 2$), apparent $[\text{S}_8]$ as a function of the advancement y of the reactions ($R = \text{Bu}^t$, experimental conditions of Figs. 1 and 2). Whatever the nature of $\text{RC}(\text{O})\text{Cl}$ (**1a–4a**), the limiting current of sulfur $i(\text{R}_1)$ increases beyond $y = 0.5$, without noticeable generation of S_8 . This catalytic effect ($\text{Ph} > \text{Me} \gg \text{Bu}^t$) was previously explained by the fast reduction (19) of $[\text{RC}(\text{O})]_2\text{S}_2$ by $\text{S}_3^{\cdot-}$ or S_8^{2-} ions.⁸ The same phenomenon



is observed when an excess of $\text{RC}(\text{O})\text{Cl}$ is poured into the solutions at y values greater than 1 (Fig. 3, curve 3); the additions of acyl chlorides to S_8 solutions ($2.6 \times 10^{-3} \text{ mol dm}^{-3} < [\text{S}_8]_0 < 3.2 \times 10^{-3} \text{ mol dm}^{-3}$), which were performed with $R = \text{Ph}, \text{Me}, \text{Bu}^t$, also lead to a great enhancement of $i(\text{R}_1)$ (Fig. 4), again in the order $\text{Ph} > \text{Me} \gg \text{Bu}^t$. Sulfur, which is quickly regenerated from step (20), can be proposed as a

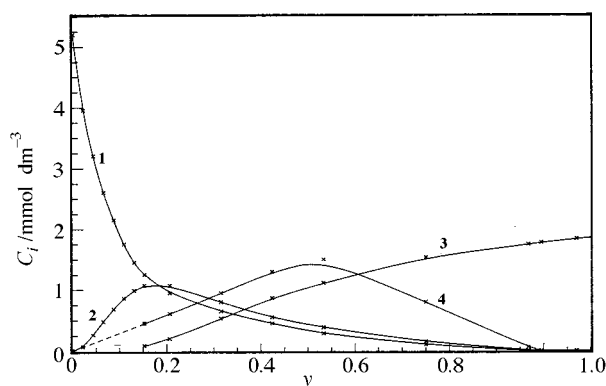


Fig. 3 Evolution of $\text{S}_3^{\cdot-}$ (1), S_8^{2-} (2), apparent S_8 (3), $\text{RC}(\text{O})\text{S}_x^-$ (4) concentrations during the addition of *tert*-butylacetyl chloride to a solution $[\text{S}_3^{\cdot-}]_T^0 = 5.17 \times 10^{-3} \text{ mol dm}^{-3}$ as a function of $y = [\text{RC}(\text{O})\text{Cl}]/[\text{S}_3^{\cdot-}]_T^0$.

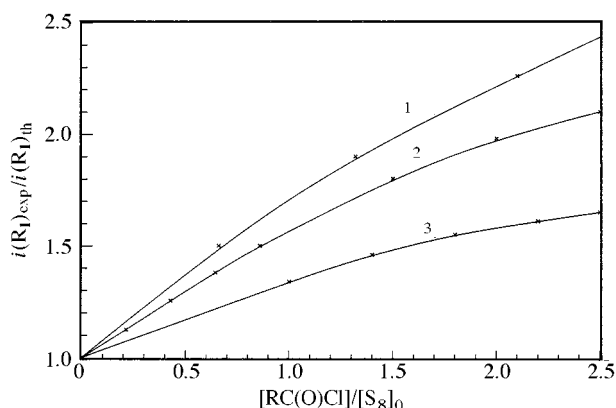
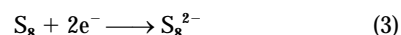


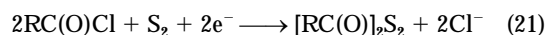
Fig. 4 Relative increase in the $i(\text{R}_1)$ reduction current of sulfur vs. $[\text{RC}(\text{O})\text{Cl}]/[\text{S}_8]_T^0$ ratio. $R = \text{Ph}$ (1), Me (2), Bu^t (3).

'mediator' for the substitution of acyl chlorides by polysulfide ions.



The electrochemical reduction of S_8 at controlled potential on the plateau of R_1 ($-1.0 \text{ V} < E < -0.8 \text{ V}$) in the presence of $\text{RC}(\text{O})\text{Cl}$ is illustrated on Figs. 5 and 6 with the experimental conditions: $[\text{S}_8]_0 = 0.83 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{Bu}^t\text{C}(\text{O})\text{Cl}]_0 = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{HCl}]_0 \approx 0.2 \times 10^{-3} \text{ mol dm}^{-3}$. [The initial concentration of hydrochloric acid estimated from $i(\text{Cl}^-)/C$ values increases with the dilution of $\text{RC}(\text{O})\text{Cl}$ because of a definite water content ($\sim 8 \times 10^{-3} \text{ mol dm}^{-3}$) in the solvent].

(i) For $0 < nF \text{ mol}^{-1} \text{ RC}(\text{O})\text{Cl} \leq 1$ (curves 2–4), the overall process (21) equivalent to reactions (3) + (20) + (17) is observed.



As soon as polysulfides S_8^{2-} appear at the electrode surface, $\text{RC}(\text{O})\text{Cl}$ in excess brings about the formation of $[\text{RC}(\text{O})]_2\text{S}_2$ by reaction (17) on the intermediate $\text{RC}(\text{O})\text{S}_x^-$ ($x = 1, 2$) ions

Table 3 Initial conditions and products of the chemical synthesis of diacyl (poly)sulfides in dimethylacetamide, R = 1–4

R	$(S_6^{2-})_0/\text{mmol}$	$(RCOCl)_0/\text{mmol}$	$[RC(O)_2S_x (\%)$			M/g	Yield ^a (%)
			x = 1	x = 2	x = 3		
Me	16.3	28	—	>99	trace ^b	1.31	62
Pr ⁱ	14.7	25	<2 ^b	96	<2 ^b	1.96	76
Bu ^t	12.6	22	—	>99	trace ^b	1.85	72
Ph	11.6	18.5	3 ^c	97	—	1.75	69

^a Yield based upon added RC(O)Cl. ^b From GC-MS. ^c From ¹H NMR.

Table 4 Electrolysis of diacyl (poly)sulfides (R = 2–4) in dimethylacetamide

R	$8(S_8)_0/\text{mmol}$	$(RCOCl)_0/\text{mmol}$	$[RC(O)]_2S_x (\%)$			M/g	Yield ^a (%)
			x = 1	x = 2	x = 3		
<i>i</i> -C ₃ H ₇	30	13.8	—	100	—	0.92	64
<i>t</i> -C ₄ H ₉	35	15.5	—	>99	trace ^b	1.12	61
C ₆ H ₅	28	14.6	2 ^c	98	—	1.35	67

^a Yield based upon added RC(O)Cl. ^b From GC-MS. ^c From ¹H NMR.

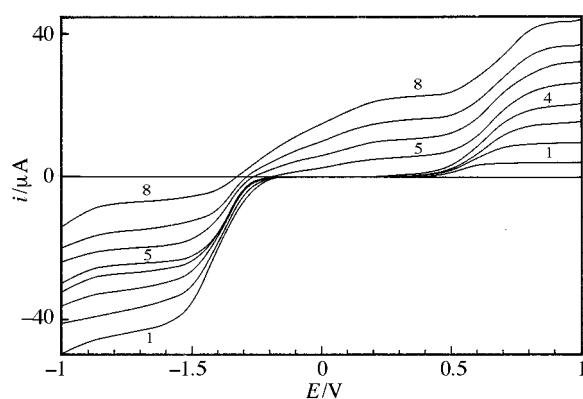


Fig. 5 Evolution of voltammograms during the electrolysis of a solution $[S_8]_0 = 0.83 \times 10^{-3} \text{ mol dm}^{-3}$ in presence of $[Bu^tC(O)Cl]_0 = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$ at $E = -0.9 \text{ V}$. $nF \text{ mol}^{-1} RC(O)Cl = 0$ (1); 0.34 (2); 0.68 (3); 1.02 (4); 1.32 (5); 1.70 (6); 2.03 (7); 2.37 (8); 2.71 (9)

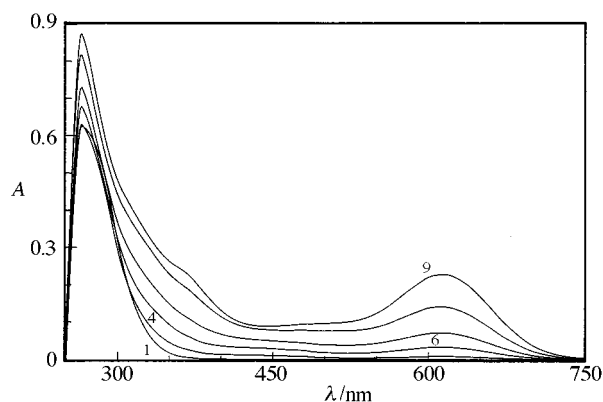
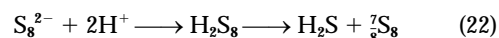


Fig. 6 Evolution of UV-VIS spectra during the electrolysis of a solution $[S_8]_0 = 0.83 \times 10^{-3} \text{ mol dm}^{-3}$; $Bu^tC(O)Cl]_0 = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$. Same conditions as for Fig. 5.

coming from the substitutions (20) and/or (14) with $S_3^{\cdot-}$ ions generated in the diffusion layer by disproportionation (4f). The cathodic R_1 wave (S_8) decreases to the benefit of the only oxidation current of Cl^- ($E_i \approx 0.65 \text{ V}$) up to $n = 1$; the solution remains colourless and the spectra practically unmodified [$\epsilon_{262}^{\text{Li}}(S_8) = 2000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; $\epsilon_{258}^{\text{Li}}(Bu^tCOS)_2 = 3000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in ref. 8].

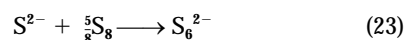
(ii) For $1 < nF \text{ mol}^{-1} RC(O)Cl < 2$ (curves 5–7), the electro-generated polysulfide ions reduce $[RC(O)]_2S_2$ species into thiocarboxylate ions [eqns. (3) + (19)] with the observation

of equilibria (10), (11) and (4) for R = alkyl; the expected species are detected on $i = f(E)$ and $A = f(\lambda)$ recordings, i.e. $S_3^{\cdot-}$ [A_{617} , $E_i(O_1) = -0.20 \text{ V}$], S_8^{2-} [A_{515} , $E_i(O_1)$], $RC(O)S_2^-$ [A_{330} , $E_i(O) \approx +0.15 \text{ V}$], $RC(O)S^-$ (A_{263}), with the simultaneous emission of H_2S whatever the nature of $RC(O)Cl$ (**1a–4a**): the protons are progressively eliminated after the formation of the H_2S_8 polysulfane which then disproportionates according to reaction (22).¹²



(iii) For $nF \text{ mol}^{-1} RC(O)Cl > 2$ (curves 8–9) the electrolysis of sulfur into polysulfides becomes predominant.

The above spectroelectrochemical results were applied on a preparative scale by two sets of experiments: direct addition of acyl chlorides to initial $S_3^{\cdot-}$ solutions [eqn. (18)]; electrolysis of sulfur in the presence of acyl chlorides [eqn. (21)]. (i) S_6^{2-} ($\equiv S_3^{\cdot-}$) ions were chemically generated from the quantitative oxidation (23) of 'anhydrous' Li_2S by sulfur.¹³

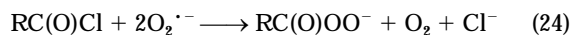


Orange S_6^{2-} ions ($\lambda_{\text{max}} = 465 \text{ nm}$) are the major species on concentrated $S_3^{\cdot-}$ solutions: for $[S_6^{2-}]_T^0 = 85 \times 10^{-2} \text{ mol dm}^{-3}$, $[S_6^{2-}]_0 = 6.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $[S_3^{\cdot-}]_0 = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ as given by K_3 (297 K) constant. $RC(O)Cl$ (**1a–3a**) in DMA were added to polysulfides at room temperature up to decoloration, which occurred at $y = [RC(O)Cl]_{\text{ad}}/[S_3^{\cdot-}]_T^0$ values less than 1 (~0.85), perhaps because of a composition of Li_2S weaker than expected. With $PhC(O)Cl$ **4a**, polysulfides $S_3^{\cdot-}/S_8^{2-}$ were totally consumed [eqn. (14)] for $y \approx 0.40$, leading only to $PhC(O)S^-$ and sulfur; the addition of $PhC(O)Cl$ was extended to $y = 0.80$ in order to carry out the second step (17). The initial conditions of the syntheses and the nature of their products have been reported in Table 3; (ii) the electrolysis of solutions $(S_8)_0 + (RCOCl)_0$ (R = 2–4) with $8(S_8)_0/(RCOCl)_0 \approx 2$ and $(RCOCl)_0 \approx 15 \text{ mmol}$ were performed in a two-compartment cell on the basis of eqn. (21), up to $1F \text{ mol}^{-1} RC(O)Cl$. Table 4 summarizes the conditions and the results of electrolyses.

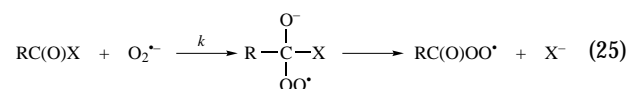
Discussion

Acyl disulfides have been synthesized by chemical¹⁴ or electrochemical¹⁵ oxidation of thiocarboxylate ions, treatment of acyl chlorides with lithium disulfide¹⁶ or sodium disulfide under phase-transfer catalysis.¹⁷ Our results establish that these compounds are readily produced by the reactions between stable $S_3^{\cdot-}$ polysulfide ions and acyl chlorides in dipolar aprotic

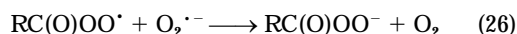
media. In a similar way, diacyl peroxides were obtained from superoxide ions and acyl chlorides⁹ in two overall steps reported as follows.^{9b} (i) nucleophilic substitution (24) of $O_2^{\cdot-}$



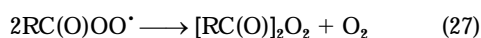
on the carbonyl carbon. The implication of an addition-elimination mechanism rather than a S_N2 one was proposed on the basis of the reactions (25) evolved with esters.¹⁸ The easy



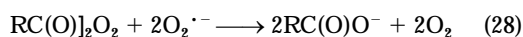
reduction (26) of the neutral acylperoxy radical by homo-



geneous electron transfer (26) then leads to $RC(O)OO^-$ ions.¹⁸⁻²⁰ The fast and concurrent formation of $[RC(O)]_2O_2$ *via* 'self reaction' (27) of $RC(O)OO^\cdot$ radicals²¹ was not observed in



the presence of $O_2^{\cdot-}$ in excess owing to reduction (28).

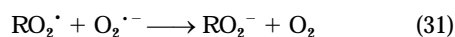


(ii) Subsequent nucleophilic substitution (29) of peroxide anions on $RC(O)Cl$. At first sight the reactivities of $O_2^{\cdot-}$ and $S_3^{\cdot-}$ ions towards acyl chlorides seem identical: as in eqn. (24), when polysulfides are in excess, $RC(O)S_2^-$ ions are initially obtained; a second step similar to eqn. (29) affords diacyl

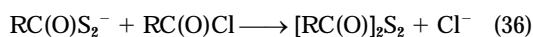


disulfides $[RC(O)]_2S_2$. These species are reducible by $S_8^{2-}/S_3^{\cdot-}$ ions into thiocarboxylates $RC(O)S^-$. However, several proposals can be advanced from the respective experimental results.

The substitution of $O_2^{\cdot-}$ on $RC(O)X$ substrates [reaction (30), $X = Cl, OC(O)R, OR'$] has always been regarded^{9b,18-20} as



analogous to that of $O_2^{\cdot-}$ on alkyl halides.²² This mechanism depends on the evolution of cyclic voltammograms of $O_2 + RX$ solutions: RO_2^- ions would quickly react with RX in excess from their generation [eqns. (30) + (31)]. An identical interpretation can be proposed to explain the electroreduction of sulfur in the presence of acyl chlorides since only diacyl disulfides were obtained for $nF \text{ mol}^{-1} RC(O)Cl \leq 1$. It would confirm the involvement of the $S_2/S_2^{\cdot-}$ system rather than S_8/S_8^{2-} one as previously claimed in redox processes.^{2,4} In that case, reactions (34) and (35) of $S_2^{\cdot-}$ ions would be faster than their

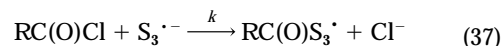


duplication into S_4^{2-} and $RC(O)S_2^-$ ions would react with

$RC(O)Cl$ before their appreciable dissociation. Nevertheless, this scheme has to be weighed against the formation of $[RC(O)]_2S_2$ by the addition of $RC(O)Cl$ to ' $RC(O)S^- + nS$ solutions'.⁸ The latter were here achieved in the first step of reactions $RC(O)Cl + S_3^{\cdot-}$ ions, the stoichiometry of which is described by eqn. (14). Several nucleophilic species can be

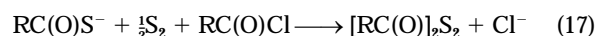


viewed: $S_3^{\cdot-}$, S_6^{2-} , S_8^{2-} . The similar reactivities of $S_3^{\cdot-}$ and $O_2^{\cdot-}$ could be consistent with the initial addition-elimination [eqn. (37)] of the radical trisulfide. With our experimental



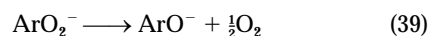
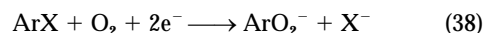
device, the rate constants of 'fast' reactions are inaccessible because of the solution transfer to the spectrophotometric cell which takes *ca.* 10 s. That the reaction is second order with respect to $S_3^{\cdot-}$ was determined in the course of slow substitutions of nitroaromatic halides^{1b} or dehalogenations of *vic*-dibromides.^{1c} This fact led us to propose S_6^{2-} ions as the effective nucleophilic $S_3^{\cdot-}$ agents. The reactivity of S_8^{2-} ions, the least reducing polysulfides, was negligible in comparison with that of S_6^{2-} , with a possible advancement of the processes^{1b,c} by the shift (4f) in the equilibrium between S_8^{2-} and $S_3^{\cdot-}$ ions.

The formation of diacyl disulfides by reactions (17) was



previously explained by an enhanced reactivity of $RC(O)S_2^-$ ions. This ' α -effect',²³ also noticed with RS_2^- ions,² is unquestionable in the example $R = Ph$ since only traces of $PhC(O)S_2^-$ were detected by voltammetry in the solutions $PhC(O)S^- + nS$. However with $R = \text{alkyl}$, acyl disulfides could instead be generated from the displacement of equilibrium (10), by the reaction of $RC(O)Cl$ with $S_3^{\cdot-}$ ions beyond the value 0.5 of the ratio $y = [RC(O)Cl]/[S_3^{\cdot-}]_T^0$. The compared nucleophilicities of $S_3^{\cdot-}$, $O_2^{\cdot-}$ and ArS_x^- ions ($Ar = 2\text{-NO}_2\text{C}_6\text{H}_4$, $4\text{-NO}_2\text{C}_6\text{H}_4$, C_6H_5 ; $x = 1, 2$) towards the same substrates in S_NAr^{1b} or S_N2 processes²⁴ decrease in the order $S_3^{\cdot-} \sim O_2^{\cdot-} > ArS_2^- > ArS^-$. From that point of view our present results indicate that the reactivity of $RC(O)S_2^-$ species can be situated at the level of the ArS_2^- one.

The dissociation of $RC(O)S_2^-$ ions is rather high in dipolar aprotic media as shown by the values of $K_5(\text{Me})$ and $K_5(\text{Bu}')$. ArO_2^- ions totally dissociate in the course of S_NAr reactions between $O_2^{\cdot-}$ and activated aromatic halides ion DMF²⁵ or DMSO⁶ yielding ArO^- ions as products [reactions (38) and (39)]. By analogy with $RC(O)S_2^-$ ions, the dissociation of



peroxy anions $RC(O)OO^-$ (and ROO^- ?) looks highly probable when $RC(O)X$ (and RX ?) species react to $O_2^{\cdot-}$ ions [eqns. (24) + (29)]. On this assumption, diacyl peroxides could be obtained by the addition of acyl chlorides to solutions of carboxylate ions saturated with oxygen.

To conclude, diacyl disulfides are conveniently produced in almost quantitative yields in the reactions between $S_3^{\cdot-}$ ions and acyl chlorides in dimethylacetamide. The process evolves *via* both the partial and concurrent formation of acyl disulfide ions and oxidation of intermediate thiocarboxylate ions. Further investigations of nucleophilic substitutions of polysulfide ions on other 'less aggressive' acylating agents than acyl chlorides, such as anhydrides, thioanhydrides and *S*-aryl thioesters, are presently in progress in our group.

Experimental

Materials and equipment

All the organic compounds were obtained from Aldrich. Lithium sulfide was purchased from Alfa-Ventron. The purification of *N,N*-dimethylacetamide and its storage after addition of tetraethylammonium perchlorate (Fluka) as supporting electrolyte (0.10 mol dm⁻³) have been reported elsewhere.²⁶ Spectroelectrochemical equipments, electrodes, the flow-through cell and the two-compartment preparative cell were previously described.^{1,6,4} The synthesized products were analysed by ¹H (200.132 MHz) and ¹³C (50.323 MHz) NMR (Bruker AC 200 spectrometer) with CDCl₃ as the solvent (internal standard Me₄Si, *J* values in Hz) and GC-MS (Hewlett-Packard 5989 A, EI 70 eV).

Generation of S₃²⁻ solutions

Sulfur (0.08–0.09 mmol S₈, 40 cm³) was electrolyzed in the flow-through cell at controlled potential on the plateau of its second reduction wave R₂ (*E* = -1.3 V) on a large gold grid electrode, according to eqn. (40). The residual acidity of the solvent was



eliminated after protonation of intermediate S₃²⁻/S₄²⁻ ions and disproportionation of H₂S_x polysulfanes into H₂S and sulfur.¹² When the absorbance reached a maximum of 617 nm, S₃²⁻ ions were the only species in solution. Before spectroelectrochemical studies their concentrations were accurately calculated from A₆₇₅ measurements, a wavelength at which S₃²⁻ absorbs alone⁴ (ε₆₇₅ = 1825 dm³ mol⁻¹ cm⁻¹).

Chemical and electrochemical syntheses

The chemical syntheses of diacyl disulfides **1b–4b** (Table 3) were carried out according to the same procedure reported on the typical example **1**: S₈²⁻ ions were generated by heating a solution (200 cm³) of Li₂S (16.3 mmol) and S₈ (81.5 mmol S) at 50 °C for 1 h under N₂ atmosphere. At room temperature, the orange–blue polysulfide ions were progressively added to CH₃C(O)Cl dissolved in 25 cm³ of DMA, up to decoloration [-28 mmol in CH₃C(O)Cl]. After filtration of sulfur, the solution was diluted with 4 vol. of 3% NaHCO₃ before extraction with diethyl ether. The organic phase was thoroughly washed with water and dried (MgSO₄). After concentration, traces of solid sulfur were eliminated by filtration at 0 °C.

The preparative electrolysis (R = **2–4**, Table 4) were also performed at room temperature; as an example, PrⁱC(O)Cl (13.8 mmol) was dissolved in 120 cm³ of the catholyte [N(Et)₄ClO₄ 0.5 mol dm⁻³ in DMA] which was then added with solid sulfur (30 mmol S); in this way the solution remained always saturated with sulfur. The potential of a large gold grid as cathode was kept between -0.60 and -0.80 V. The current retained a great intensity (220–240 mA) as a result of catalytic effects on the reduction of sulfur with both reagents RC(O)Cl and products [RC(O)]₂S₂. With R = alkyl, the end of the process was detected by the appearance of the red colour of S₈²⁻ polysulfides coming from reduction (19) of diacyl disulfides and equilibria (10) + (4). After filtration of excess sulfur and solid N(Et)₄Cl, the reaction medium was treated in the same way as for chemical syntheses.

The oily products [RC(O)]₂S_x (R = Me, Prⁱ, Bu^t) were purified by column chromatography on silica gel (light petroleum–diethyl ether as eluent, 80:20); dibenzoyl disulfide was recrystallized from 1,2-dichloroethane.

Diacetyl disulfide (1b). δ_H 2.54 (6 H, s); δ_C 28.8 (2 C) and 189.5 (2 C); *m/z* 150 (M⁺, <2%) and 43 (100).

Bis(dimethylacetyl) disulfide (2b). δ_H 1.28 (12 H, d, *J* 6.9) and 2.96 (2 H, septet, *J* 6.9); δ_C 18.9 (4 C), 41.9 (2 C) and 195 (2 C); *m/z* 206 (M⁺, <2%), 71 (77) and 43 (100). (PrⁱCO)₂S (Table 3

~2% from GC-MS); *m/z* 174 (M⁺, <2%), 71 (100) and 43 (84); (PrⁱCO)₂S₃ (Table 3 ~2% from GC-MS); *m/z* 238 (M⁺, <2%), 71 (95) and 43 (100).

Bis(trimethylacetyl) disulfide (3b). δ_H 1.37 (18 H, s); δ_C 27.0 (6 C), 46.8 (2 C) and 199 (2 C); *m/z* 234 (M⁺, <2%), 85 (53), 57 (100) and 41 (11).

Dibenzoyl disulfide (4b). Mp 135–136 °C (lit.,²⁷ 136–136.5 °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 (2 C), 134 (2 C) and 186 (2 C); direct introduction mode *m/z* 274 (M⁺, 4%), 105 (50), 77 (100) and 51 (25). (C₆H₅CO)₂S (Tables 3 and 4 ~2–3%) from δ_H 8.06 (4 H, *J* 7.4).

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