Reactivity of electrogenerated polysulfide ions towards acyl thioanhydrides and anhydrides 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 electrogenerated polysulfide ions $S_3^{\bullet -}$ ($\rightleftharpoons S_6^{2-}$) in *N*,*N*-dimethylacetamide has been followed by spectroelectrochemistry of a series of RC(O)X species: thioanhydrides X = SC(O)R (R = CH_3 **1a**, C_6H_5 **2a**) and anhydrides X = OC(O)R (R = CH_3 **3b**, *n*-C_3H_7 **4b**, *t*-C_4H_9 **5b**, C_6H_5 **6b**). With thioanhydrides two steps were evidenced: (i) formation of $RC(O)S^-$ in equilibrium with $RC(O)S_2^-$ from both fast substitution at the trigonal carbon and exclusion from the nucleofugic anion X^-: (ii) subsequent reaction of $RC(O)S_2^-$ on substrates leading to diacyl disulfides. With anhydrides the first step only occurs at a slower rate. The electrolysis of sulfur in the presence of **1a** or **2a** allowed the preparative scale formation of $RC(O)S_2C(O)R$ as isolated products from the 'electrochemical insertion of sulfur' in diacyl monosulfides.

Réactivité des ions polysulfures électrogénérés dans le diméthylacétamide vis-à-vis des thioanhydrides et anhydrides d'acides carboxyliques La réactivité des ions polysulfures $S_3^{\bullet -}$ ($\rightleftharpoons S_6^{2-}$) électrogénérés dans le *N*,*N*-diméthylacétamide a été suivie par spectroélectrochimie vis-à-vis d'une série de dérivés RC(O)X: thioanhydrides X = SC(O)R (R = CH_3 **1a**, C_6H_5 **2a**), anhydrides X = OC(O)R (R = CH_3 **3b**, *n*-C_3H_7 **4b**, *t*-C_4H_9 **5b**, C_6H_5 **6b**). Avec les thioanhydrides, deux étapes sont mises en évidence: (i) formation des ions $RC(O)S^-$ et $RC(O)S_2^-$ en équilibre du fait de la substitution sur le carbone trigonal et de l'obtention de l'anion nucléofuge X^-; (ii) réaction ultérieure des ions $RC(O)S_2^-$ sur les substrats conduisant aux diacyldisulfures. Avec les anhydrides seule la première étape s'effectuant plus lentement est observée. L'électrolyse du soufre en présence des espèces **1a** ou **2a** réalisée au niveau préparatif a permis d'isoler les diacyldisulfures issus de 'l'insertion électrochimique du soufre' sur les diacylmonosulfures.

As reported recently,[1] acyl chlorides 'instantaneously' react with $S_3^{\bullet -}$ ($\rightleftharpoons S_6^{2-}$) ions in *N*,*N*-dimethylacetamide, a dipolar aprotic medium, to produce diacyldisulfides (62–75% yield). Two successive steps were evidenced by spectroelectrochemistry: (i) initial substitution (eqn 1) of the leaving group, with concurrent equilibria (eqns 2 and 3) as established by direct addition of sulfur to thiocarboxylate ions:[2]

$$RC(O)Cl + 2\ S_3^{\bullet -} \rightarrow RC(O)S^- + 5/2\ S_2 + Cl^- \qquad (1)$$

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

$$2\ RC(O)S^- + S_2 \rightleftharpoons 2\ RC(O)S_2^- \qquad (3)$$

and (ii) subsequent reaction (eqn 4) of $RC(O)S_2^-$ species:

$$RC(O)S_2^- + RC(O)Cl \rightarrow [RC(O)]_2S_2 + Cl^- \qquad (4)$$

Eqns 1 and 4 are analogous to those implied in the formation of diacylperoxides from RC(O)X [X = Cl, OC(O)R] and superoxide ions $O_2^{\bullet -}$ in aprotic media.[3]

We report here on the relative reactivities of electrogenerated $S_3^{\bullet -}$ ions towards acylating agents: 'thioanhydrides' $[RC(O)]_2S$ (R = CH_3 **1a**, C_6H_5 **2a**) and anhydrides $[RC(O)]_2O$ (R = CH_3 **3b**, *n*-C_3H_7 **4b**, *t*-C_4H_9 **5b**, C_6H_5 **6b**). Reactions were followed at 20 °C by UV-vis absorption spectrophotometry coupled with stationary voltammetry.

Results

Sulfur-polysulfide ion characteristics in DMA

The partial dissociation (eqn 5) of cyclooctasulfur S_8 into S_2 molecules was recently proposed by our group in dimethylacetamide:[4]

$$S_8 \rightleftharpoons 4\ S_2 \qquad (5)$$

$$K_1(297\ K) = [S_2]^4/[S_8] = 10^{-7}\ mol^3\ dm^{-9} \qquad (6)$$

In aprotic media such as DMA, sulfur reduces in two two-electron steps with respect to the cyclic form S_8[4] [waves R1, $E_{1/2} = -0.40$ V *vs.* reference and R2, $E_{1/2} = -1.10$ V, experimental value $i(R1)/[S_8]_0 = 34\ \mu A\ mmol^{-1}\ dm^3$] on a rotating gold-disc electrode. In the presence of excess of sulfur we expect the initial single-electron transfer $S_2 + e^- \rightarrow S_2^{\bullet -}$ to be followed by the reaction of S_2 with the dimeric S_4^{2-} ions, up to the formation of S_6^{2-} ($\rightleftharpoons S_3^{\bullet -}$) or S_8^{2-} species.[4,5] The stable product of the overall electrolysis of S_8 at controlled potential on R1 (eqn 10) is the blue anion-radical $S_3^{\bullet -}$ ($\lambda_{max} = 617$ nm, $\varepsilon_{max} = 4390\ dm^3\ mol^{-1}\ cm^{-1}$) through the disproportionation (eqn 8) of the carmine red S_8^{2-} ions ($\lambda_{max1} = 515$ nm, $\varepsilon_{max1} = 3800\ dm^3\ mol^{-1}\ cm^{-1}$; $\lambda_{max2} = 360$ nm, $\varepsilon_{max2} = 9000\ dm^3\ mol^{-1}\ cm^{-1}$):

$$S_8 + 2\ e^- \rightarrow S_8^{2-} \qquad (7)$$

$$S_8^{2-} \underset{b}{\overset{f}{\rightleftharpoons}} 2S_3^{\bullet -} + S_2 \qquad (8)$$

$$K_2(297\ K) = [S_3^{\bullet -}]^2[S_2]/[S_8^{2-}] = 1.7 \times 10^{-6}\ mol^2\ dm^{-6} \qquad (9)$$

$$S_8 + 8/3\ e^- \rightarrow 8/3\ S_3^{\bullet -} \qquad (10)$$

$S_3^{\bullet -}$ ions are in equilibrium with their dimer S_6^{2-} ($\lambda_{max} = 465$ nm, $\varepsilon_{max} = 3100\ dm^3\ mol^{-1}\ cm^{-1}$):

$$S_6^{2-} \rightleftharpoons 2\ S_3^{\bullet -} \qquad (11)$$

$$K_3 = [S_3^{\cdot -}]^2/[S_6^{2-}] = 0.043 \text{ mol dm}^{-3} \qquad (12)$$

UV-vis absorption spectra (ε_i/dm^3 mol^{-1} cm^{-1}) of S_8, S_8^{2-}, S_6^{2-}, $S_3^{\cdot -}$ ions between 250 and 750 nm were previously reported.[5] In dilute solutions $[S_6^{2-}]$ remains low with respect to $[S_3^{\cdot -}]$ (*i.e.*, 16% at total concentration $[S_3^{\cdot -}]_0^T = [S_3^{\cdot -}] + 2\ [S_6^{2-}] = 5.0 \times 10^{-3}$ mol dm^{-3}). S_8^{2-} and S($-1/3$) ions oxidize (O1) and reduce (R2) at the same potentials [$E_{1/2}$(O1) $= -0.20$ V; $E_{1/2}$(R2) $= -1.10$ V].

Reactivity of $S_3^{\cdot -}$ ions with the thioanhydrides 1a, 2a

As observed with acyl chlorides,[1] the addition of the thioanhydrides **1a**, **2a** to a sulfur solution greatly enhances the limiting current of the reduction wave R1: $i(\text{R1})_{\text{exp.}}/i(\text{R1})_{\text{th.}} =$ 2.3 (**1a**) and 2.0 (**2a**) for $[(\text{RCO})_2\text{S}]/[S_8]_0 = 2.0$. This homogeneous catalytic effect (eqns 7 and 13) agrees with the fast regeneration (eqn 13) of sulfur in the course of the reaction of polysulfide ions with substrates RC(O)X [X = Cl[1], SC(O)R] in the diffusion layer:

$$\text{RC(O)X} + S_8^{2-} \rightarrow \text{RC(O)S}^- + 7/8\ S_8 + X^- \qquad (13)$$

Here the nucleofuge X^- and the substitution product would be the same species: RC(O)S$^-$. This was verified by the addition of a concentrated solution of thioanhydride **1a** or **2a** in DMA (2.0–7.0 $\times 10^{-2}$ mol dm^{-3}) to $S_3^{\cdot -}$ ions of total concentrations $[S_3^{\cdot -}]_0^T$ close to 5.0×10^{-3} mol dm^{-3}. Fig. 1 and 2 show the evolution of $A = f(\lambda)$ and $i = f(E)$ as a function of the ratio $y = [\text{RC(O)X}]/[S_3^{\cdot -}]_0^T$ for the example $R = CH_3$ with $[S_3^{\cdot -}]_0^T = 5.22 \times 10^{-3}$ mol dm^{-3}. As long as y remains below ≈ 0.15 (Fig. 1*a*), A_{617} ($S_3^{\cdot -}$) decreases in favor of A_{515} and A_{360} (S_8^{2-}) with an isosbestic point at 540.5 nm; there is no sign of R1 (S_8) on any of the voltammograms. The stoichiometry (eqn 15) is the same as with acyl chlorides: sulfur coming from the substitution (eqn 14) totally reacts with $S_3^{\cdot -}$ ions in excess according to eqn 8b:

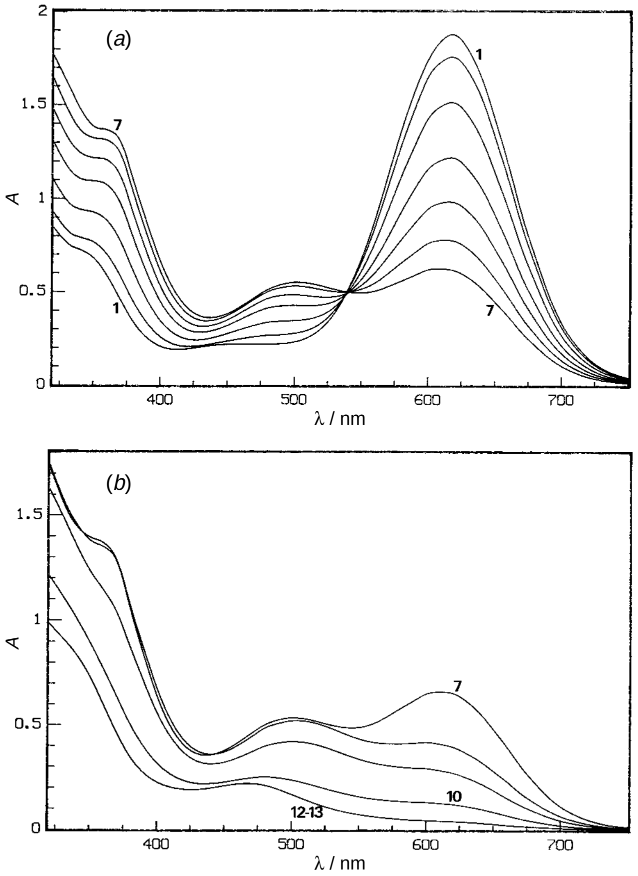

Fig. 1 (*a*) Evolution of UV-vis spectra during the addition of diacetyl sulfide **1a** to an S($-1/3$) solution, $[S_3^{\cdot -}]_0^T = 5.22 \times 10^{-3}$ mol dm^{-3}. The thickness of the cell was 0.1 cm; $y = [(\text{RCO})_2\text{S}]/[S_3^{\cdot -}]_0^T = 0$ (curve 1), 0.03 (2), 0.05 (3), 0.08 (4), 0.11 (5), 0.14 (6), 0.15 (7). (*b*) The same as (*a*) with $y = 0.15$ (7), 0.24 (8), 0.33 (9), 0.50 (10), 0.71 (11), 0.84 (12), 1.27 (13)

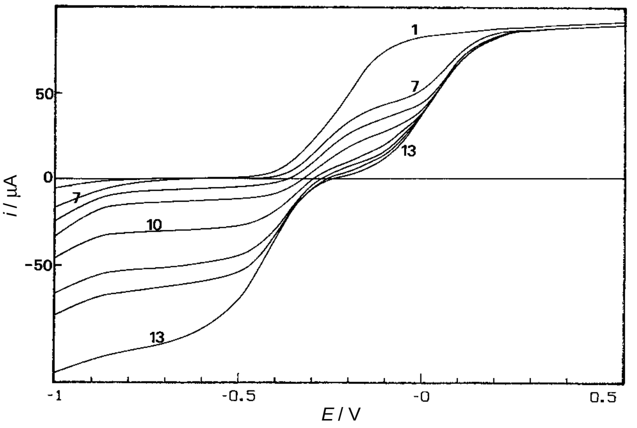

Fig. 2 Evolution of voltammograms during the reaction of diacetyl sulfide **1a** with S($-1/3$) ions. Same conditions as for Fig. 1. Rotating gold-disc electrode, $\Omega = 1000$ rev min^{-1}, diameter = 2 mm; *E vs.* Ag/AgCl, KCl satd in DMA–N(Et)$_4$ClO$_4$ (0.1 mol dm^{-3}) reference

$$[\text{RC(O)}]_2\text{S} + 2\ S_3^{\cdot -} \rightarrow \text{RC(O)S}^- + 5/2\ S_2 + \text{RC(O)S}^- \qquad (14)$$

$$[\text{RC(O)}_2]_2\text{S} + 7\ S_3^{\cdot -} \rightarrow 2\ \text{RC(O)S}^- + 5/2\ S_8^{2-} \qquad (15)$$

At the same time, the oxidation wave of RC(O)S$^-$/RC(O)S$_2^-$ ions (the electroanalytic process eqns 16 + 3 + 17 previously described,[2] $E_{1/2} = +0.09$ V) increases at the expense of the $S_8^{2-}/S_3^{\cdot -}$ one ($E_{1/2} = -0.20$ V).

$$2\ \text{RC(O)S}^- \rightarrow [\text{RC(O)}]_2S_2 + 2\ e^- \qquad (16)$$

$$2\ \text{RC(O)S}_2^- \rightarrow [\text{RC(O)}]_2S_2 + S_2 + 2\ e^- \qquad (17)$$

The subsequent consumptions of the two $S_3^{\cdot -}$ ions and S_8^{2-} by a shift in the equilibrium (eqn 8f) ($0.15 < y < 0.5$) permits the detection of sulfur by the growth of its cathodic wave R1 ($E_{1/2} = -0.40$ V). For $y = 0.5$ (stoichiometry of eqn 14), the equilibria (eqns 2 and 3) bear out the remaining presence of polysulfide ions in the solution; the $S_3^{\cdot -}$ and S_8^{2-} concentrations calculated from K_1, K_2, K_3 and the constants[2] K_4, K_5 lead to A_{617} and A_{515} values close to the experimental ones ($\pm 10\%$):

$$K_4 = [\text{RC(O)S}_2^-][S_3^{\cdot -}]^2/[\text{RC(O)S}^-]^2[S_2]^3$$
$$= (12 \pm 2) \text{ dm}^6 \text{ mol}^{-2} \qquad (18)$$

$$K_5 = [\text{RC(O)S}_2^-]^2/[\text{RC(O)S}^-]^2[S_2]^1 = (48 \pm 4) \text{ dm}^3 \text{ mol}^{-1} \qquad (19)$$

With further additions of $[\text{RC(O)}]_2\text{S}$ ($0.5 < y < 1.0$, curves 10–13), $S_3^{\cdot -}$ and S_8^{2-} ions continue to be consumed [decrease in A_{617}, A_{515} and i(O)] but these species cannot be totally eliminated because of the weak oxidation (eqn 2) of the nucleofugic RC(O)S$^-$ ions. Low concentrations of $CH_3C(O)S_2^-$ ions (eqn 3) are revealed in the spectra (Fig. 1*b*, curves 12, 13) by their characteristic absorbances[2] ($\lambda_{\text{max1}} =$ 336 nm, $\varepsilon_{\text{max1}} = 4800$ dm^3 mol^{-1} cm^{-1}; $\lambda_{\text{max2}} = 467$ nm, $\varepsilon_{\text{max2}} = 800$ dm^3 mol^{-1} cm^{-1}). i(R1) continues to rise with values greater than those of generated S_8, due to a catalytic effect analogous to eqns 7 + 13, which was previously noticed when diacyldisulfides were added to sulfur.[2] At $y = 1$, the oxidation current of RC(O)S$^-$/RC(O)S$_2^-$ ions is in agreement with that resulting from the overall eqn 20.

$$2\ [\text{RC(O)}]_2\text{S} + 2\ S_3^{\cdot -} \rightarrow [\text{RC(O)}]_2S_2 + 2\ S_2 + 2\text{RC(O)S}^- \qquad (20)$$

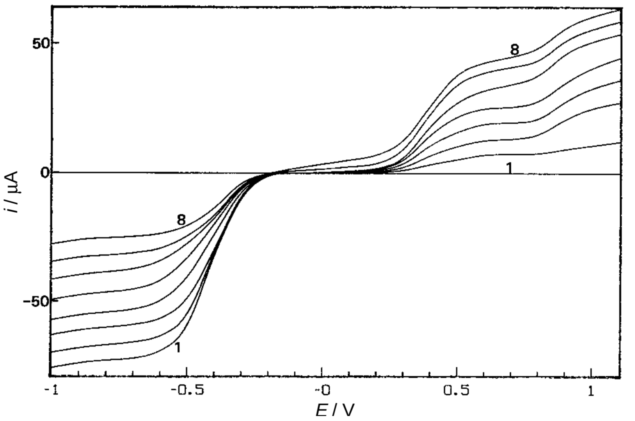

Fig. 3 Evolution of voltammograms during the electrolysis of a solution with $[S_8]_0 = 1.05 \times 10^{-3}$ mol dm^{-3} in the presence of dibenzoylsulfide, $[\mathbf{2a}]_0 = 1.74 \times 10^{-3}$ mol dm^{-3} at $E = -1.0$ V *vs.* reference *n* F mol^{-1} **2a** = 0 (curve 1), 0.37 (2), 0.75 (3), 1.12 (4), 1.49 (5), 1.86 (6), 2.24 (7), 2.62 (8)

With the addition of sulfur, $C_6H_5C(O)S^-$ ions are not oxidized in accordance with eqn 2[2] and the residual formation of $RC(O)S_2^-$ ions (eqn 3) is only detected by their electrocatalytic and kinetic oxidation wave[2] (eqns 16, 3 + 17, $E_{1/2} = +0.35$ V). The evolution of $i = f(E)$ and $A = f(\lambda)$ for the reaction of $[C_6H_5C(O)]_2S$ with $S_3^{\cdot -}$ are the same as with R = alkyl ($0 < y < 1$) except that $S_8^{2-}/S_3^{\cdot -}$ ions totally disappear at $y = 0.5$.

The electrochemical reduction of sulfur ($E \approx -1.0$ V) in the presence of the thioanhydrides **1a**, **2a**, which confirms the preceding results, is illustrated in Fig. 3 with the experimental conditions: $[(C_6H_5CO)_2S]_0 = 1.74 \times 10^{-3}$ mol dm^{-3}, $[S_8]_0 = 1.05 \times 10^{-3}$ mol dm^{-3}. For $0 < n$ F mol^{-1} **2a** < 2 (curves 2–6) the decrease of the catalytic current *i*(R1) goes with the increase of the anodic waves of the $RC(O)S_2^-$ ($E_{1/2} = +0.35$ V) and $RC(O)S^-$ ($E_{1/2} = +0.72$ V) ions.[2] Two steps were observed when RC(O)Cl + S_8 solutions were electrolyzed in the same way:[1] (i) initial formation (eqn 21) of diacyldisulfide ($0 < n < 1$), with only appearance of the oxidation current of Cl^- ions on the voltammograms:

$$2\ RC(O)X + S_8 + 2\ e^- \rightarrow [RC(O)]_2S_2 + 3/4\ S_8 + 2\ X^- \qquad (21)$$

and (ii) reduction (eqn 22) of $[RC(O)]_2S_2$ by polysulfide ions ($1 < n < 2$), with the growth of the anodic wave of $RC(O)S^-$ ions:

$$[RC(O)]_2S_2 + S_8 + 2\ e^- \rightarrow 2\ RC(O)S^- + (S_8) \qquad (22)$$

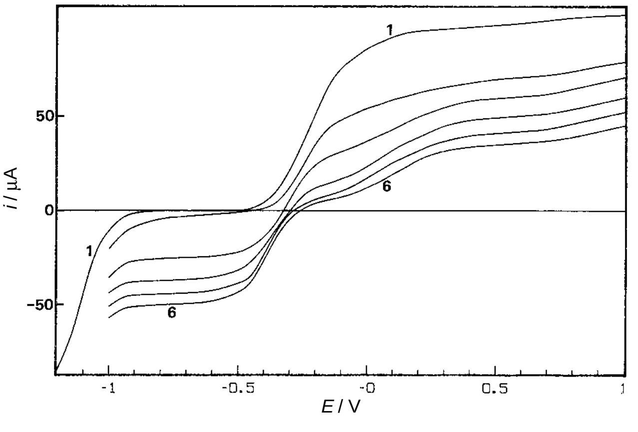

Fig. 4 Evolution of voltammograms during the addition of trimethylacetic anhydride **5b** to an S(−1/3) solution, $[S_3^{\cdot -}]_0^T = 5.69 \times 10^{-3}$ mol dm^{-3}. $y = [(RCO)_2S]/[S_3^{\cdot -}]_0^T = 0$ (curve 1), 0.14 (2), 0.25 (3), 0.47 (4), 0.79 (5), 1.22 (6)

In our particular case X^- species are $RC(O)S^-$ ions, which are then generated on the basis 1 $RC(O)S^-$/1 F. The overall process looks like the noteworthy 'electrochemical insertion' (eqn 23) of sulfur into thioanhydrides:

$$2\ [RC(O)]_2S + S_2 + 2\ e^- \rightarrow [RC(O)]_2S_2 + 2\ RC(O)S^- \qquad (23)$$

Beyond $n = 2$, $S_8^{2-}/S_3^{\cdot -}$ ions result from the reduction of sulfur (growth of A_{617}, A_{515} and *i*(O) at $E_{1/2} = -0.20$ V, curves 7, 8). The electrolysis of $[RC(O)]_2S$ **1a**, **2a** with sulfur added as a 'mediator' at a ratio of 8 $[S_8]_0/[RC(O)]_2S \approx 2.5$ were performed on a preparative scale $\{n = 1$ F mol^{-1} $[RC(O)]_2S\}$. $[RC(O)]_2S_2$ was the only product isolated (R = CH_3, yield 48%; R = C_6H_5, 74%).

Reactivity of $S_3^{\cdot -}$ ions with anhydrides 3b–6b

An analogous study was carried out with anhydrides as substrates. Whatever the nature of R (**3b**–**6b**) the enhancement of the reduction current of sulfur was only observed at R2 potentials with the addition of $[RC(O)]_2O$: $i(R1 + R2)_{exp.}/i(R1 + R2)_{th.} \approx 1.5$ for $[(RCO)_2O]/[S_8]_0 = 2.0$. As noticed on the first wave R1 with thioanhydrides, this observation agrees with the catalytic effect (eqns 24 + 25), which implies here the more reducing agents S_4^{2-}.[4,6] These last species were not generated in the present study by quantitative electrolysis of sulfur.

$$S_8 + 4\ e^- \rightarrow 2\ S_4^{2-} \qquad (24)$$

$$[RC(O)]_2O + S_4^{2-} \rightarrow RC(O)S^- + 3/8\ S_8 + RCO_2^- \qquad (25)$$

Thiocarboxylate ions (R = **3**–**6**) proved to be practically unreactive towards anhydrides at room temperature: the maximal absorbance $A_{262} = 1.90$ and the oxidation wave of a solution of $[CH_3C(O)S^-]_0 = 2.90 \times 10^{-3}$ mol dm^{-3} ($E_{1/2} = +0.31$ V) only decreased by 5% in the presence of $[CH_3C(O)]_2O = 3.0 \times 10^{-3}$ mol dm^{-3} whereas no spectroelectrochemical changes were noticed for $[(t\text{-}C_4H_9CO)_2S^-] = 2.70 \times 10^{-3}$ mol dm^{-3} with $[(t\text{-}C_4H_9CO)_2O]_{ad} = 3.60 \times 10^{-3}$ mol dm^{-3}. In the presence of sulfur, the reactions were limited: for $[CH_3C(O)S^-]_0 = 2.27 \times 10^{-3}$ mol dm^3; 8 $[S_8]_0 = 11.0 \times 10^{-3}$ mol dm^{-3}; $[(CH_3CO)_2O]_{ad} = 8.5 \times 10^{-3}$ mol dm^{-3}, the anodic current of $RC(O)S_2^-/RC(O)S^-$ ions ($E_{1/2} = +0.05$ V) retained 60% of its initial value at equilibrium after 10 min while *i*(R1) increased because of the catalytic effect (eqns 7 + 13) due to the partial formation of $[RC(O)]_2S_2$. Under the same conditions $C_6H_5C(O)S^- + S_8$ solutions were unreactive towards benzoic anhydride. When anhydrides **3b**–**6b** were added to $S_3^{\cdot -}$ ions (R = $t\text{-}C_4H_9$, Fig. 4), the evolutions of the spectra and voltammograms for $0 < y < 0.5$ were identical to those observed with thioanhydrides (*i.e.*, Figs. 1*a* and 1*b*, curves 1–10) or acyl chlorides;[1] however, except for R = C_6H_5, the reactions slowed down for *y* greater than 0.3: as an example for $[S_3^{\cdot -}]_0^T = 5.50 \times 10^{-3}$ mol dm^{-3}, $y = 0.40$, equilibria were attained after 1 min with R = $n\text{-}C_3H_7$ and 8 min with R = $t\text{-}C_4H_9$. Beyond $y = 0.5$, the addition of alkyl substrates only partially consumed $RC(O)S^-/RC(O)S_2^-$ ions and at a slow rate: *e.g.*, from curve 6 of Fig. 4 which was recorded at $y = 1.22$ after 15 min, 80% of anionic species remained in solution.

Discussion

Diacyldisulfides are usually synthesized by chemical[7] or electrochemical[8] oxidation of thiocarboxylate ions and reactions of acyl chlorides with Li_2S_2[9] or Na_2S_x under PTC conditions.[10] Our results establish that these species are readily obtained by the reactions of thioanhydrides with $S_3^{\bullet -}$ polysulfide ions at room temperature, as observed with acyl chlorides.[1] In both cases, thiocarboxylate ions coming from the fast nucleophilic substitution on the carbonyl carbon react in the presence of sulfur with the organic substrates RC(O)X. The formation of $[RC(O)]_2S_2$ species can be explained by an enhanced reactivity of intermediate $RC(O)S_2^-$ ions compared to $RC(O)S^-$. This α effect,[11] already displayed with RS_2^- ions,[5] probably competes with the displacement of the equilibrium (eqn 2f) by consumption of the stronger $S_3^{\bullet -}$ nucleophiles. The lower reactivity of anhydrides in general compared to that of acyl chlorides[12] only allows access to $RC(O)S^-$ ions. With respect to thioanhydrides, the same observation agrees with 'the relative weakness of the overlapping of the C(2p) and S(3p) orbitals in the carbon–sulfur bond' as noted by Cronyn *et al.*[13] Thioanhydrides can be easily prepared by acylation of thiocarboxylate ions.[14,15] These more stable species appear to be as efficient acylating agents as acyl chlorides in aprotic media.

Experimental

Materials and equipment

Diacetyl sulfide **1a** and anhydrides **3b**–**6b** were obtained from Aldrich and used as received (purity > 98%). Dibenzoyl sulfide **2a** (mp 45–47 °C, lit.[15] 47–48 °C) was previously synthesized[2] by addition of benzoyl chloride to electrogenerated thiobenzoate ions from thiobenzoic acid. Spectroelectrochemical experiments were carried out in DMA (Aldrich) with added tetraethylammonium perchlorate (Fluka, 0.1 mol dm^{-3}) at 20 °C with equipment, electrodes and the flow-through cell previously described.[4] Potential values refer to Ag/AgCl, KCl satd in $DMA/N(Et)_4ClO_4$ (0.1 mol dm^{-3}). Analysis of diacyl disulfides was performed by GC-MS (Hewlett-Packard 5989 A) and NMR spectroscopy (Bruker AC 200 spectrometer, $CDCl_3$ as solvent, J values in Hz at 200.132 and 50.323 mHz for ^1H and ^{13}C NMR, respectively).

Generation of S(−1/3) ions

S(−1/3) solutions (40 cm^3) were prepared at concentrations near 5×10^{-3} mol dm^{-3} before addition of concentrated RC(O)X substrates in DMA ($V_{max} = 4$ cm^3) by electroreduction of sulfur at controlled potential (R2, $E \approx -1.4$ V) on a large gold-grid electrode.[4] $S_3^{\bullet -}$ ($\rightleftharpoons S_6^{2-}$) ions were the only species in solutions when A_{617} reached its maximum value.

Preparative electrolysis

$[CH_3C(O)]_2S_2$ and $[C_6H_5C(O)]_2S_2$ were obtained by electrolysis of sulfur (-0.7 V $< E < -0.5$ V) with added homologous diacyl monosulfides up to 1 F mol^{-1} $[RC(O)]_2S$ (eqn 23). The experimental conditions (two-compartment cell, electrodes, procedure and purification) were the same as with acyl chlorides.[1] The intensity remained at a high value (200–250 mA) in the course of the electroreductions because of catalytic effects with both substrates $[RC(O)]_2S$ and products $[RC(O)]_2S_2$.

Diacetyl disulfide. Diacetyl sulfide: 1.18 g (10 mmol); S_8: 0.77 g (24 mmol S). Product: diacetyl disulfide (0.36 g, 48%); 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).

Dibenzoyl disulfide. Dibenzoyl sulfide: 0.72 g (3 mmol); S_8: 0.24 g (7.5 mmol S). Product dibenzoyl disulfide (0.41 g, 74%); mp 135–136 °C (lit.:[16] 136–136.5 °C); δ_H 7.53–7.75 (6 H, m) and 8.13 (4 H, d, $^3J_{1H}$ 7.4 Hz); 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).

References

1 J. Robert, M. Anouti, M. Abarbri and J. Paris, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1759.
2 J. Robert, M. Anouti and J. Paris, *J. Chem. Soc., Perkin Trans. 2*, 1997, 473.
3 (*a*) R. Johnson, *Tetrahedron Lett.*, 1976, **5**, 331; (*b*) D. T. Sawyer, J. J. Stamp and K. A. Menton, *J. Org. Chem.*, 1983, **48**, 337; (*c*) J. P. Stanley, *J. Org. Chem.*, 1980, **45**, 1413; (*d*) A. Le Berre and Y. Berguer, *Bull. Soc. Chim. Fr.*, 1966, **7**, 2368.
4 G. Bosser and J. Paris, *New J. Chem.*, 1995, **19**, 391 and references therein.
5 G. Bosser, M. Anouti and J. Paris, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1993.
6 J. Paris and V. Plichon, *Electrochim. Acta*, 1982, **27**, 1501.
7 R. L. Franck and J. R. Blegen, *Org. Synth. Coll.*, 1955, **3**, 116–118.
8 Y. Hirabayashi and T. Mazume, *Bull. Chem. Soc., Jpn.*, 1966, **39**, 1971.
9 J. A. Gladysz, V. K. Wong and B. S. Jick, *Tetrahedron*, 1979, **35**, 2329.
10 (*a*) M. Kodomari, M. Fukuda and S. Yoshitomi, *Synthesis*, 1981, **8**, 637; (*b*) J. X. Wang, W. Cui, Y. Hu and K. Zhao, *Synth. Commun.*, 1995, **25**, 889.
11 J. E. Dixon and T. C. Bruice, *J. Am. Chem. Soc.*, 1972, **94**, 2052 and references therein.
12 J. March, *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, Wiley, New York, 1992, p. 409.
13 M. W. Cronyn, M. Chang Pin and R. A. Wall, *J. Am. Chem. Soc.*, 1955, **77** 3031.
14 (*a*) E. E. Reid, *Organic Chemistry of Bivalent Sulfur*, Chemical Publishing, New York, 1962, vol. 4, pp. 11–58; (*b*) H. Böhme and H. P. Steudel, *Liebigs Ann. Chem.*, 1969, **730**, 121.
15 M. Mikolajczyk, P. Kielbasinski and H. M. Schiebel, *J. Chem. Soc., Perkin Trans. 1*, 1976, 564.
16 C. Christophersen and P. Carlsen, *Tetrahedron*, 1976, **32**, 745.

Received 28*th May* 1997; *Paper* 7/06743G