Nucleophilic substitution of *S*-phenyl thiol esters by electrogenerated polysulfide ions in *N*,*N*-dimethylacetamide

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The reactivity of electrogenerated $S^{\frac{1}{3}-}$ polysulfide ions $S_3^{\cdot -}$ ($\rightleftharpoons S_6^{2-}$) towards *S*-phenyl thiol esters RC(O)SPh [R = Me (1), Et (2), Pr^i (3)] has been followed by spectroelectrochemistry in *N*,*N*-dimethylacetamide at 24 °C. With 1 and 2 reactions readily lead to thiocarboxylate ions and phenyltetrasulfanide ions, PhS_4^-, from the nucleofugic benzenethiolate ions in presence of sulfur. With 3 kinetic studies imply that S_6^{2-} species are the nucleophilic $S^{\frac{1}{3}-}$ agents rather than $S_3^{\cdot -}$ radical anions in a second order rate process (k = 30 ± 3 dm^3 mol^{-1} s^{-1}).

S-alkyl and *S*-aryl carbothioates ('thiol esters') are useful intermediates in organic synthesis, as they have a higher reactivity towards nucleophiles than their oxygen homologues. Their acylating properties have been notably used in lactonisations, leading to macrocyclic natural products[1] and the preparation of acylstannanes,[2] whereas superoxide ions substitute on dithioic *S*,*S*′-diesters.[3]

We recently reported on the reactions between $S_3^{\cdot -}$ polysulfide ions and RC(O)X species [X = Cl;[4] SC(O)R and OC(O)R[5]] in dipolar aprotic medium. Two successive and fast steps were evidenced with acyl chlorides and thioanhydrides: initial substitution [reaction (1)] followed by reaction (2) of thiocarboxylate

$$RC(O)X + 2S_3^{\cdot -} \longrightarrow RC(O)S^- + \tfrac{5}{2}S_2 + X^- \qquad (1)$$

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

ions in the presence of sulfur, leading to diacyl disulfides. With anhydrides, the first step occured at a lower rate.

We examine here the reactivity of electrogenerated $S_3^{\cdot -}$ ions towards a series of *S*-phenyl thiol esters RC(O)SPh [R = Me (**1**), Et (**2**), Pr^i (**3**)] in *N*,*N*-dimethylacetamide (DMA). Both the known spectroelectrochemical characteristics of sulfur/polysulfide ions and the behaviour of the nucleofugic benzenethiolate ions in the presence of sulfur enabled the reactions to be followed by UV–VIS absorption spectrophotometry coupled with stationary voltammetry.

Results

Characteristics of sulfur/polysulfides and benzenethiolate–sulfur solutions in DMA

The partial dissociation of cyclooctasulfur S_8 into S_2 molecules (~50% at $[S_8]_T = 1.5 \times 10^{-3}$ mol dm^{-3}) in dimethylacetamide was recently proposed by our group[6] [equilibrium (3), eqns. (4)

$$S_8 \rightleftharpoons 4S_2 \qquad (3)$$

$$K_1(297\ \mathrm{K}) = [S_2]^4[S_8]^{-1} = 10^{-7}\ \mathrm{mol^3\ dm^{-9}} \qquad (4)$$

and (5)]. As in other aprotic media, sulfur reduces in DMA in

$$[S_8]_T = [S_8] + \tfrac{1}{4}[S_2] \qquad (5)$$

two bielectronic steps with respect to total S_8[6] (waves R$_1$, $E_{\frac{1}{2}} = -0.40$ V *vs.* ref.† and R$_2$, $E_{\frac{1}{2}} = -1.10$ V on a rotating gold-disc electrode). In the course of its electrolysis at controlled potential on R$_1$ [reaction (6), probably through the initial elec-

$$S_8 + 2e^- \longrightarrow S_8^{2-} \qquad (6)$$

tron transfer[6] $S_2 + e^- \rightarrow S_2^{\cdot -}$ followed by the reactions of S_2 on the dimeric form S_4^{2-}, then on S_6^{2-} up to S_8^{2-}], S_8^{2-} ions [λ_{max1} = 515 nm, ε_{max1} = 3800 dm^3 mol^{-1} cm^{-1}; λ_{max2} = 360 nm, ε_{max2} = 9000 dm^3 mol^{-1} cm^{-1}; ε_{617} = 300 dm^3 mol^{-1} cm^{-1}; $E_{\frac{1}{2}}$(R) = −1.10 V, $E_{\frac{1}{2}}$(O) = −0.20 V] disproportionate into $S_3^{\cdot -}$ ions [λ_{max} = 617 nm, ε_{max} = 4390 dm^3 mol^{-1} cm^{-1}; $E_{\frac{1}{2}}$(R) = −1.10 V, $E_{\frac{1}{2}}$(O) = −0.20 V] and sulfur [equilibrium (7), eqn. (8)]. The total consumption of

$$S_8^{2-} \underset{b}{\overset{f}{\rightleftharpoons}} 2S_3^{\cdot -} + S_2 \qquad (7)$$

$$K_2\ (297\ \mathrm{K}) = [S_3^{\cdot -}]^2[S_2][S_8^{2-}]^{-1} = 1.7 \times 10^{-6}\ \mathrm{mol^2\ dm^{-6}} \qquad (8)$$

sulfur leads to $S^{\frac{1}{3}-}$ polysulfide ions, $S_3^{\cdot -}$ and S_6^{2-} (λ_{max} = 465 nm, ε_{max} = 3100 dm^3 mol^{-1} cm^{-1}) in equilibrium [equilibrium (9),

$$S_6^{2-} \rightleftharpoons 2S_3^{\cdot -} \qquad (9)$$

eqn. (10)]. In dilute solutions, $[S_6^{2-}]$ remains low in comparison

$$K_3(297\ \mathrm{K}) = [S_3^{\cdot -}]^2[S_6^{2-}]^{-1} = 0.043\ \mathrm{mol\ dm^{-3}} \qquad (10)$$

to $[S_3^{\cdot -}]$ (*e.g.* $[S_6^{2-}] = 0.42 \times 10^{-3}$ mol dm^{-3} at total concentration $[S_3^{\cdot -}]_T^0 = [S_3^{\cdot -}] + 2[S_6^{2-}] = 5.0 \times 10^{-3}$ mol dm^{-3}).

In DMA we showed that thiolate ions react with sulfur in two parallel and fast ways:[7] (*i*) weak oxidation [reaction (11)] giving

$$2RS^- + 3S_2 \longrightarrow RS_2R + 2S_3^{\cdot -} \qquad (11)$$

disulfides and polysulfide ions and (*ii*) dominating reaction (12)

$$2RS_{x-1}^- + S_2 \rightleftharpoons 2RS_x^- \qquad (12)$$

yielding successive formation of RS_x^- ions (R = alkyl, x = 2–5; R = aryl, x = 2–4):

$$K_{(x)} = [RS_x^-]^2[RS_{x-1}^-]^{-2}[S_2]^{-1} \qquad (13)$$

The reactivity of RS$^-$ ions towards sulfur is the same as that of 'thionucleophilic' Nu species such as CN$^-$, SO_3^{2-} and Ar$_3$P, leading to SNu products, with the hypothetical opening of the S_8 ring as the rate-determining step.[8] By analogy with RS$^-$/O$_2$ processes,[9] we suggested[7a] a very different mechanism involving initial monoelectronic transfer [reaction (14)] followed by coup-

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† All potentials are expressed in comparison to the reference electrode (ref. 6) Ag/AgCl(s), KCl sat. in DMA/N(Et)$_4$ClO$_4$ 0.1 mol dm^{-3}.

Table 1 Spectroelectrochemical characteristics and successive formation constants of PhS_x^- ions in *N*,*N*-dimethylacetamide

PhS_x^-	λ_{max}/nm	ε_{max}/dm^3 mol cm^{-1}	$E_{\frac{1}{2}}$(O)/V	$K_{(x)}{}^a$/mol dm^{-3}
PhS^-	309	18200	+0.16	—
PhS_2^-	310^b	3200^b	−0.03	3.4×10^9
PhS_3^-	460	400	+0.10	1.2×10^7
PhS_4^-	460	900	+0.10	5.8×10^4

^{a} $K_{(x)}$ at 298 K and ionic strength = 0.1 mol dm^{-3}. ^{b} From ref. 7*b*.

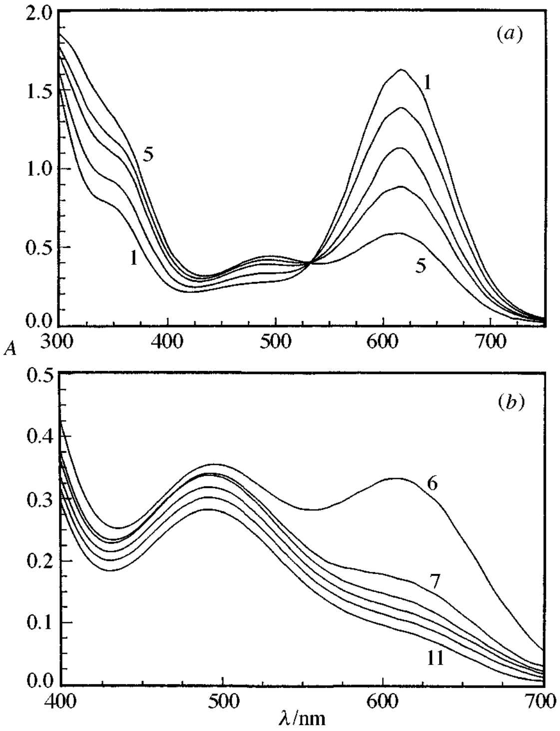

Fig. 1 Evolution of UV–VIS spectra during the addition of *S*-phenyl thioacetate to a $S_3^{\cdot -}$ solution $[S_3^{\cdot -}]_T^0 = 4.30 \times 10^{-3}$ mol dm^{-3}. (*a*) y = $[RC(O)SPh]_{ad.}/[S_3^{\cdot -}]_T^0$ = 0 (1); 0.04 (2); 0.08 (3); 0.13 (4); 0.21 (5). (*b*) y = 0.30 (6); 0.38 (7); 0.46 (8); 0.72 (9); 0.89 (10); 1.36 (11). Scan rate: 1000 nm min^{-1}.

$$RS^- + S_2 \longrightarrow RS^{\cdot} + S_2^{\cdot -} \qquad (14)$$

lings between $RS^{\cdot}$ and $S_2^{\cdot -}$ radicals into RS_3^- ions (reducible into RS_2^- by RS^- in excess), RS_2R and polysulfide ions. With less reductive aromatic thiolates ArS^- ($Ar = C_6H_5$, 4-$CH_3C_6H_4$), oxidation (11) was practically unobserved. For values of x greater than 2, RS_x^- ions were characterized[7a] by a visible band (λ_{max} = 460–470 nm) and their oxidation wave into RS_2R. Table 1 summarizes spectroelectrochemical parameters for $C_6H_5S_x^-$ ions, and their successive formation constants $K_{(x)}$. Whatever the nature of R, RS_4^- ions partly disproportionate according to the key equilibrium (15) [with eqn. (16)], at the junction of concurrent eqns. (11) and (12).[7a]

$$2RS_4^- \rightleftharpoons RS_2R + 2S_3^{\cdot -} \qquad (15)$$

$$K_4 = [RS_2R][S_3^{\cdot -}]^2[RS_4^-]^{-2} \qquad (16)$$

When RS_2R and $S_3^{\cdot -}$ were mixed in the ratio 1 : 2, spectra and voltammograms were the same as those obtained by mixing sulfur and thiolate ions in the proportion $[S]_{ad.}/[RS^-]_0 = 3$. In the present study, PhS_4^- ions will be directly generated by electroreduction of diphenyl disulfide into benzenethiolate ions, then stoichiometric addition of sulfur as previously described,[7a] and the value K_4 (298 K) = 2.0×10^{-4} mol dm^{-3} (R = Ph) will be taken again.

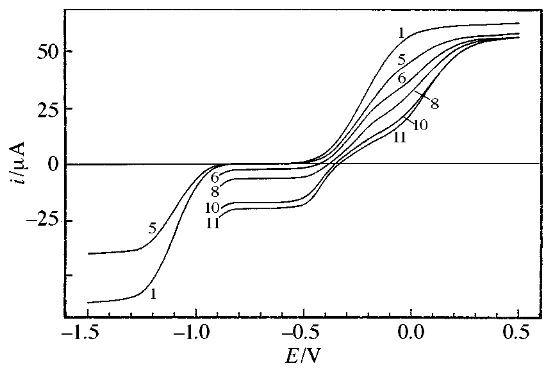

Fig. 2 Evolution of voltammograms during the reaction of *S*-phenyl thioacetate with $S_3^{\cdot -}$ ions. Same conditions as for Fig. 1. Rotating gold-disc electrode, Ω = 1000 rev min^{-1}, diameter = 2mm. *E vs.* reference Ag/$AgCl_{(s)}$, KCl sat. in DMA/$N(Et)_4ClO_4$ 0.1 mol dm^{-3}. Scan rate: 10 mV s^{-1}.

Reactivity of $S_3^{\cdot -}$ ions with *S*-phenyl thiol esters

With *S*-phenyl thioacetate (**1**) and *S*-phenyl thiopropionate (**2**) esters the fast reactions were followed at 24 °C by the same evolutions of $A = f(\lambda)$ and $i = f(E)$ recordings as shown in Figs. 1(*a*), 1(*b*) and 2 when $CH_3C(O)SPh$ was added to a solution $[S_3^{\cdot -}]_T^0 = 4.30 \times 10^{-3}$ mol dm^{-3}. (*i*) As long as the ratio y = $[RC(O)SPh]_{ad.}/[S_3^{\cdot -}]_T^0$ remained less than 0.25 [Figs. 1(*a*) and 2, curves (2)–(5)], the consumption of $S_3^{\cdot -}$ ions was evidenced by the fall in anodic and cathodic currents [$E_{\frac{1}{2}}$(O) = −0.20, $E_{\frac{1}{2}}$(R) = −1.10 V], and A_{617} decreased to the benefit of A_{490} through an approximate isosbestic point at 525 nm without any appearance of sulfur (no wave R_1 on voltammograms), in agreement with reactions (7b) and (17) and (18), summarized by the overall reaction (19).

$$RC(O)SPh + 2S_3^{\cdot -} \longrightarrow RC(O)S^- + PhS^- + \tfrac{5}{2}S_2 \qquad (17)$$

$$PhS^- + \tfrac{3}{2}S_2 \longrightarrow PhS_4^- \qquad (18)$$

$$2S_3^{\cdot -} + S_2 \longrightarrow S_8^{2-} \qquad (7b)$$

$$RC(O)SPh + 4S_3^{\cdot -} \longrightarrow RC(O)S^- + PhS_4^- + S_8^{2-} \qquad (19)$$

Sulfur coming from substitution (17) reacts preferentially with PhS^- rather than $S_3^{\cdot -}$ ions, up to PhS_4^-: as an example, for $[S_3^{\cdot -}]_T^0 = 4.30 \times 10^{-3}$ mol dm^{-3} and $[RC(O)SPh]_{ad.}$ = $0.537_5 \times 10^{-3}$ mol dm^{-3} ($y = \frac{1}{8}$), K_1, K_2, K_3 and $K_{(x)}$ constants for reaction (17) give calculated concentrations at equilibrium: $[S_3^{\cdot -}]_T = 2.17_5 \times 10^{-3}$, $[S_2] = 8.1 \times 10^{-6}$, $[S_8^{2-}] = 0.525 \times 10^{-3}$ and $[PhS_4^-] = 0.537 \times 10^{-3}$ mol dm^{-3}, with $[PhS_4^-] \approx [S_8^{2-}]$ bearing out reaction (19). The maximal absorption of S_8^{2-} ions at 515 nm was slightly shifted to shorter wavelengths (≈490 nm) by the presence of PhS_4^- ions. From[7] $\varepsilon_{490}(S_8^{2-}) \approx 3500$ and ε_{490}-$(PhS_4^-) \approx 800$ dm^3 mol^{-1} cm^{-1}, variations $\Delta([S_3^{\cdot -}]_T)/\Delta[S_8^{2-}]$ = -4.0 ± 0.2 ($0 < y < 0.2$) satisfied reaction (19). (*ii*) For $0.25 < y < 0.50$ [curves (6)–(8)], the consumption of $S_3^{\cdot -}$ and S_8^{2-} ions [probably through the shift (7f) because S_8^{2-} ions are less nucleophilic species than $S_3^{\cdot -}$ ones[10]] entailed both decreases of A_{617} and A_{490}, and growths of the oxidation current of PhS_4^- ions [$E_{\frac{1}{2}}$(O) = +0.10 V] and of the reduction wave R_1 of sulfur [$E_{\frac{1}{2}}$(R) = −0.40 V], according to reaction (20).

$$RC(O)SPh + 2S_3^{\cdot -} \longrightarrow RC(O)S^- + S_2 + PhS_4^- \qquad (20)$$

However for $y = 0.5$, $S_3^{\cdot -}$ and S_8^{2-} ions were not eliminated because of their partial regeneration by the extensive disproportionation [reaction (15)] of PhS_4^- ions followed by reaction (7b): *e.g.* with initial conditions $[PhS_4^-]_0 = [S_2]_0 = 2.15 \times 10^{-3}$ mol dm^{-3}, at equilibrium $[PhS_4^-] = 0.55 \times 10^{-3}$, $[S_2] = 1.49 \times 10^{-3}$, $[S_3^{\cdot -}]_T = 0.276 \times 10^{-3}$ and $[S_8^{2-}] = 0.66 \times 10^{-3}$ mol dm^{-3} from K_2 and K_4 constants; (*iii*) beyond $y = 0.5$ [curves (9)–(11)] the evolution of VIS spectra was strictly the same as that observed with the direct addition of RC(O)SPh to a solution $[\mathrm{PhS_4^-}]_0 = 2.15 \times 10^{-3}$ mol dm^{-3}: the substrate in excess displaces equilibrium (15) by the reaction (20) with polysulfide ions.

In the presence of sulfur, RC(O)S$^-$ ions weakly lead to the formation [reaction (21), with eqn. (22)] of RC(O)S$_2^-$ species as

$$2\mathrm{RC(O)S^-} + \mathrm{S_2} \underset{\mathrm{b}}{\overset{\mathrm{f}}{\rightleftharpoons}} 2\mathrm{RC(O)S_2^-} \qquad (21)$$

$$K_5 = [\mathrm{RC(O)S_2^-}]^2[\mathrm{RC(O)S^-}]^{-2}[\mathrm{S_2}]^{-1} \qquad (22)$$

previously reported.[11] For example, with R = CH$_3$ and $[\mathrm{CH_3C(O)S^-}]_0 = 2[\mathrm{S_2}]_0 = 2.15 \times 10^{-3}$ mol dm^3 RC(O)S$_2^-$ reaches 17% at equilibrium from[11] K_5 (293 K) = 48 dm^3 mol^{-1}. As observed with thiolate ions,[7] RC(O)S$^-$ species directly oxidize into disulfides [reaction (23), R = CH$_3$, $E_{\frac{1}{2}}$(O) = +0.31 V], or at

$$2\mathrm{RC(O)S^-} - 2\mathrm{e^-} \longrightarrow [\mathrm{RC(O)}]_2\mathrm{S_2} \qquad (23)$$

the lower potentials of RC(O)S$_2^-$ ions [$E_{\frac{1}{2}}$(O) ≈ +0.09 V] in the presence of traces of sulfur, by the electrocatalytic process[11] given by reactions (21) + (24).

$$2\mathrm{RC(O)S_2^-} - 2\mathrm{e^-} \longrightarrow [\mathrm{RC(O)}]_2\mathrm{S_2} + \mathrm{S_2} \qquad (24)$$

We verified that CH$_3$C(O)S$^-$/CH$_3$C(O)S$_2^-$ ions, which were generated by initial electroreduction of thiolacetic acid,[11] are unreactive towards the substrate CH$_3$C(O)SPh {($i = f(E)$ and $A = f(\lambda)$ recordings of an initial solution $[\mathrm{CH_3C(O)S^-}]_0 = 1.45 \times 10^{-3}$ mol dm^{-3}, $[\mathrm{S}]_0 = 7.85 \times 10^{-3}$ mol dm^{-3} were unmodified by the addition of $[\mathrm{CH_3C(O)SPh}] = 3.25 \times 10^{-3}$ mol dm^{-3}}; so in the course of the overall reaction (20) ($0 < y < 0.5$, Fig. 2) the anodic currents of PhS$_4^-$ ($E_{\frac{1}{2}}$ = +0.10 V) and CH$_3$C(O)S$^-$/CH$_3$C(O)S$_2^-$ ions ($E_{\frac{1}{2}}$ ≈ +0.09 V) progressively took the place of $\mathrm{S_3^{\cdot-}}/\mathrm{S_8^{2-}}$ one ($E_{\frac{1}{2}}$ = −0.20 V).

During the progress y of the fast reaction between *S*-phenyl thiopropionate ester (**2**) and an initial solution $[\mathrm{S_3^{\cdot-}}]_\mathrm{T}^0 = 4.30 \times 10^{-3}$ mol dm^{-3}, $[\mathrm{S_3^{\cdot-}}]_\mathrm{T}$ was accurately determined ($0 < y < 1.5$) with A_{675} measurements, a wavelength at which the radical anion alone absorbs [ε_{675} ($\mathrm{S_3^{\cdot-}}$) = 1825 dm^3 mol^{-1} cm^{-1}]; $[\mathrm{S_8}]_\mathrm{T}$ was estimated ($y > 0.3$) from $i(\mathrm{R_1})$ values by use of the coefficient $i(\mathrm{R_1})/[\mathrm{S_8}]_\mathrm{T} = 34.0 \pm 0.5$ μA mmol^{-1} dm^3 depending on our working electrode; $[\mathrm{S_8^{2-}}]$ was deducted from spectrophotometric parameters at 490 and 617 nm with a significant precision for $0 < y < 0.5$. Fig. 3 shows the changes of these 'experimental' concentrations, and of all the calculated values ‡ from constants K_1–K_4 and equations of conservation of sulfur, thiolester and charges as a function of y. It summarizes the previously described steps: (*i*) $0 < y \leqslant 0.25$ [eqn. (19)] without any detection of sulfur and maximal formation of S$_8^{2-}$ ions for $y \approx 0.25$; (*ii*) quantitative generation of RC(O)S$^-$ ions up to $y = 0.5$ [eqn. (20)]; (*iii*) $y > 0.5$: partial consumption of PhS$_4^-$ ions from the shift of equilibrium (15), with an advancement for $y = 1$ of 70% with respect to the balance [reaction (25)] of eqns. (15) + (20).

$$\mathrm{RC(O)SPh} + \mathrm{S_3^{\cdot-}} \longrightarrow \mathrm{RC(O)S^-} + \tfrac{1}{2}\mathrm{PhS_2Ph} + \mathrm{S_2} \qquad (25)$$

Kinetic studies of the reaction of $\mathrm{S}^{\frac{1}{3}-}$ ions with *S*-phenyl thioisobutyrate

Probably owing to steric hindrance, *S*-phenyl thioisobutyrate reacted slowly with $\mathrm{S}^{\frac{1}{3}-}$ ions. In that case the kinetic study was carried out at 24 °C on the recordings of A_{617} *vs.* time after the addition of substrate **3** to $[\mathrm{S_3}]_\mathrm{T}^0$ solutions [eqn. (26)].

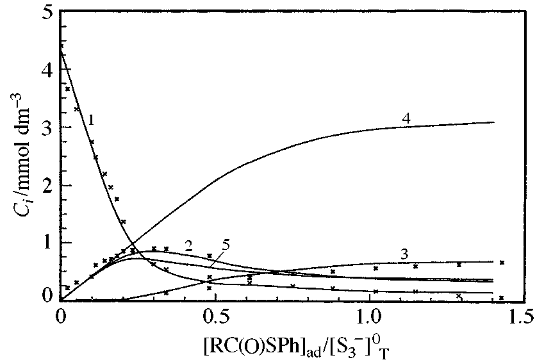

Fig. 3 Calculated curves of concentrations $[\mathrm{S_3^{\cdot-}}]_\mathrm{T}$ (1), S$_8^{2-}$ (2), S$_8$ (3), RC(O)S$^-$ (4), PhS$_4^-$ (5) as a function of $y = [\mathrm{RC(O)SPh}]_\mathrm{ad.}/[\mathrm{S_3^{\cdot-}}]_\mathrm{T}^0$ compared with experimental values during the addition of *S*-phenyl thioproprionate to a $\mathrm{S}^{\frac{1}{3}-}$ solution $[\mathrm{S_3^{\cdot-}}]_\mathrm{T}^0 = 4.30 \times 10^{-3}$ mol dm^{-3}

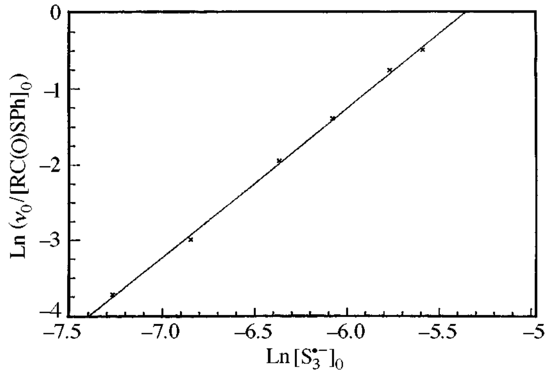

Fig. 4 Kinetic studies of the reaction of *S*-phenyl thioisobutyrate with $\mathrm{S}^{\frac{1}{3}-}$ at 24 °C. Variation of the initial rate as a function of $[\mathrm{S_3^{\cdot-}}]_0$.

$$A_{617}^t/l = \varepsilon_3[\mathrm{S_3^{\cdot-}}]_t + \varepsilon_8[\mathrm{S_8^{2-}}]_t \qquad (26)$$

The order n of the reaction concerning $\mathrm{S_3^{\cdot-}}$ was obtained by the initial-rate method. As long as the ratio $\Delta[\mathrm{RC(O)SPh}]/[\mathrm{S_3^{\cdot-}}]_\mathrm{T}^0$ remains less than $\frac{1}{4}$, the overall reaction (19) can be considered

$$\mathrm{RC(O)SPh} + 4\mathrm{S_3^{\cdot-}} \longrightarrow \mathrm{RC(O)S^-} + \mathrm{PhS_4^-} + \mathrm{S_8^{2-}} \qquad (19)$$

alone, without any absorbance of PhS$_4^-$ and S$_6^{2-}$ ions at 617 nm.[7]

In nucleophilic processes, the reactivity of the least reducing polysulfide ions S$_8^{2-}$ [12] was negligible in comparison to that of $\mathrm{S}^{\frac{1}{3}-}$ species;[10] here again the rate of reaction (19) greatly decreased when **3** was added to a solution $\mathrm{S_3^{\cdot-}}$ saturated with sulfur. ($[\mathrm{S_8}]_\mathrm{T} \approx 9 \times 10^{-3}$ mol dm^{-3}), so the rate equation can be expressed as eqns. (27) and (28). Constant K_3 and the linked variations of $[\mathrm{S_3^{\cdot-}}]_t$ and $[\mathrm{S_8^{2-}}]_t$ [reaction (19)] easily give eqn. (29).

$$v_t = -\frac{1}{4}\frac{\mathrm{d}[\mathrm{S_3^{\cdot-}}]_\mathrm{T}}{\mathrm{d}t} = k_\mathrm{obs}[\mathrm{RC(O)SPh}]_t[\mathrm{S_3^{\cdot-}}]_t^n \qquad (27)$$

$$\ln(v_0/[\mathrm{RC(O)SPh}]_0) = \ln k_\mathrm{obs} + n\ln[\mathrm{S_3^{\cdot-}}]_0 \qquad (28)$$

$$v_0 = -\frac{1}{4\varepsilon_3 - \varepsilon_8}\left(1 + \frac{4[\mathrm{S_3^{\cdot-}}]_0}{K_3}\right)\frac{1}{l}\left(\frac{\mathrm{d}A_{617}}{\mathrm{d}t}\right)_{t \longrightarrow 0} \qquad (29)$$

The determination of v_0 for six pairs of values ($[\mathrm{S_3^{\cdot-}}]_\mathrm{T}^0$, $[\mathrm{RC(O)SPh}]_0$) enabled us to obtain (Fig. 4) $n = 1.98 \pm 0.08$ and $k_\mathrm{obs} = 710 \pm 40$ dm^6 mol^{-2} s^{-1} at an ionic strength equal to 0.1 mol dm^{-3}. The hypothesis of a trimolecular process in the rate-determining step is relatively improbable. This fact, which was previously noticed in the course of the slow reactions between $\mathrm{S}^{\frac{1}{3}-}$ ions and nitroaromatic halides[10a] or vicinal dibromides,[10b]

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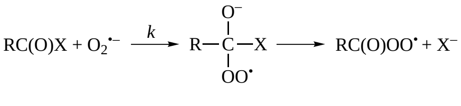
‡ The minor formation of acyl disulfide ions according to equilibrium (21) was not taken into account in our iterative calculations.

led us to propose also S_6^{2-} ions as the effective nucleophilic agents in substitutions (20). It can be attributed to the more localized charge on terminal sulfur atoms of S_6^{2-} compared to $S_3^{\cdot -}$ ones, as proposed by Meyer *et al.*[13] using calculations by the extended Hückel method. The rate is thus characterized by the constant $k = k_{obs} \times K_3$ with k (**3**) = 30 ± 3 $dm^3\ mol^{-1}\ s^{-1}$.

Discussion

When *S*-methyl thiobutanoate and *S*-ethyl thioacetate, or ethyl and phenyl acetate were added at 24 °C to $S_3^{\cdot -}$ solutions in DMA in the ratio $[RC(O)XR']/[S_3^{\cdot -}]_T^0 = 5$ (X = S, O) reactions did not occur to any appreciable extent. The reactivity of $S^{\frac{1}{3}-}$ ions towards *S*-phenyl thiolesters in *N*,*N*-dimethylacetamide can be compared to that of $O_2^{\cdot -}$ ions on *O*-phenyl esters in pyridine[14] [$k(CH_3CO_2Ph) = 160$, $k(CH_3CO_2Et) = 1.1 \times 10^{-2}$ $dm^3\ mol^{-1}\ s^{-1}$; 20 °C ?] or DMF[15] {$k[4\text{-}ClC_6H_4OC(O)Ph] = 25$, $k(C_6H_5CO_2Ph) = 3.0$ $dm^3\ mol^{-1}\ s^{-1}$; 20 °C}. On the basis of cyclic voltammetry experiments,[14] the implication of an initial addition–elimination mechanism (30) was proposed for



$$RC(O)X + O_2^{\cdot -} \xrightarrow{k} R\text{—}\overset{O^-}{\underset{OO^\cdot}{C}}\text{—}X \longrightarrow RC(O)OO^\cdot + X^-$$

$RC(O)X + O_2^{\cdot -}$ reactions evolved with esters, followed by the reduction of the acylperoxyradical [reaction (31)]. Owing to the

$$RC(O)OO^\cdot + O_2^{\cdot -} \longrightarrow RC(O)OO^- + O_2 \qquad (31)$$

presumed high nucleophilicity of $RC(O)OO^-$ anions, the final formation of carboxylate ions[14,15] was ascribed to subsequent reactions (32) and (33).

$$RC(O)OO^- + RC(O)X \longrightarrow [RC(O)]_2O_2 + X^- \qquad (32)$$

$$[RC(O)]_2O_2 + 2O_2^{\cdot -} \longrightarrow 2RC(O)O^- + 2O_2 \qquad (33)$$

The net rate depended on the stability of the leaving group $X^-[k(Ar\ O^-) \gg k(R'O^-)]$ as observed in the present study with thiol esters $[k(PhS^-) \gg k(RS^-)]$. Reactions of acyl chlorides and 'thioanhydrides'[5] with $S^{\frac{1}{3}-}$ ions occurred in two overall steps (1) and (2), respectively analogous to (30) + (31) and (32), but $RC(O)S_2^-$ ions greatly dissociate into $RC(O)S^-$ and sulfur [eqn. (21b)].[11] The only formation of diacyl disulfides by the addition of RC(O)Cl to $RC(O)S^- + S_2$[11] [eqn. (2)] was explained by an enhanced reactivity of minory $RC(O)S_2^-$ ions with respect to thiocarboxylate ions 'α-effect'.[16] In the same conditions [step (2)], anhydrides $[RC(O)]_2O$ were practically unreactive[5] as shown here with *S*-phenyl thiol esters. So, in the course of $RC(O)OR' + O_2^{\cdot -}$ processes, ions RCO_2^- ions could result from the dissociation of $RC(O)OO^-$ species rather than from eqns. (32) + (33). This hypothesis agrees with the dispute about an intermediate diacyl peroxide *en route* to the acid RCO_2H when superoxide ions reacted with phenylbenzoate esters in benzene.[17]

To conclude, in dipolar aprotic medium thiocarboxylate ions are readily obtained from S_6^{2-} ions and the more efficient acylating agents *S*-phenyl thiol esters than *O*-homologues, probably due to the weak conjugation between sulfur and the carbonyl group.[18]

Experimental

Materials and equipment

All the organic compounds of commercial origin (purity > 98%) were used as received except for thiolacetic acid which was distilled under dry nitrogen just before handling. The purification of *N*,*N*-dimethylacetamide and its storage after addition of $N(Et)_4ClO_4$ 0.1 mol dm^{-3}, spectroelectrochemical equipment, electrodes and the thermostatted (24.0 ± 0.5 °C) flow-through cell have been described previously.[6]

Generation of $S^{\frac{1}{3}-}$ solutions and procedures

Initial $S^{\frac{1}{3}-}$ solutions (40 cm^3) were obtained by exhaustive electrolysis [reaction (34)] of sulfur (0.1–0.65 mmol S) at controlled

$$S_8 + \tfrac{8}{3}e^- \longrightarrow \tfrac{8}{3}S_3^{\cdot -} \qquad (34)$$

potential of a large gold grid electrode on the plateau of the R_2 wave ($E = -1.3$ V). $S_3^{\cdot -}$ ions in equilibrium with S_6^{2-} [reaction (9)] were the only species in solution when A_{617} reached a maximum.

The stoichiometry of the fast overall (19) and (20) processes was studied by the progressive addition of concentrated solutions of RC(O)SPh **1** or **2** in DMA ($v_{max} = 4$ cm^3) to $S^{\frac{1}{3}-}$ ions ($4.2 \times 10^{-3} < [S_3^{\cdot -}]_T^0 < 4.60 \times 10^{-3}$ mol dm^{-3}).

Initial rate measurements were based on A_{617} changes *vs.* time when a small volume ($v_{max} = 1$ cm^3) of *S*-phenyl thioisobutyrate in DMA was added to each of six solutions $0.77 \times 10^{-3} < [S_3^{\cdot -}]_T^0 < 3.18 \times 10^{-3}$ mol dm^{-3} ($0.37 > y > 0.18$) at 24 °C; the transfer of the reaction medium to the spectrophotometric cell (1 mm pathlength) took about 15 s, whereas reaction half-times with respect to $S_3^{\cdot -}$ were such as 230 s > $t_{\frac{1}{2}}$ > 70 s.

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Paper 7/07562F
Received 20*th October* 1997
Accepted 12*th December* 1997